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Hydride Complexes

The chemistry and current significance of covalent hydrogen compounds of transition metals are discussed.

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Hydrogen is a ubiquitous chemical element, which can be brought into combination with most other elements. It behaves as a positive ion in strong acids, and occurs as a negative ion in combination with very electropositive metals. It forms hard alloy-like hydrides with the lanthanides and transition metals, and covalent compounds with most of the remaining elements. Nevertheless, until very recently it appeared incapable of forming covalent or ionic bonds with the transition metals, such as chromium, iron, cobalt, nickel, copper, and the platinum metals.

The last decade has seen a change in all of this. Numerous complex compounds of the general type $[MH_xL_y]$ have been discovered. Here M is a transition metal and L is a ligand (*1*) attached to the metal. The ligands L are not usually all of the same kind, and although most hydride complexes are mononuclear—that is, contain only one metal atom in the molecule, as given in the formula—a few are di- and polynuclear, especially when L is carbon monoxide.

These complexes contain covalent M–H bonds which usually have little, if any, tendency to ionize as hydrides. This covalency confers on many of the hydrido- complexes a surprising resistance to hydrolysis by water. Furthermore, transition metals, especially the platinum metals, can take as ligands unsaturated hydrocarbons, carbon monoxide, and related substances. Thus they can bring these together with hydrogen and so catalyze a great variety of useful reactions, which might well include the reduction of nitrogen gas to ammonia as it occurs in biological systems—as vital to life as photosynthesis itself.

In this article I summarize the various types of hydride complexes and their interestingly unique properties (*2*).

Historically, the subject reaches back to 1844, when Wurtz (*3*) obtained an ill-defined, unstable red-brown hydrated copper hydride, usually formulated CuH, by the reduction of aqueous copper sulfate with hypophosphorous acid. When prepared in pyridine, this hydride contains pyridine, but the nature of the substance is still rather uncertain. In the 1920's, Weichselfelder and Thiede (*4*) found that hydrogen was absorbed during the reaction, under hydrogen, of phenylmagnesium bromide with the halides of the lighter transition metals in ether. The dark oily or black products liberated the hydrogen again on treatment with acid, and formulas such as CrH_3, FeH_2, FeH_6, CoH_2, and NiH_2 were assigned them. They are, however, very complex and ill defined.

The first reasonably well defined, but nonetheless very unstable, hydride complexes of transition metals were $[FeH_2(CO)_4]$ and $[CoH(Co)_4]$, discovered in 1931 by Hieber and his coworkers (*5*). These substances were long a mystery because they are acidic, and for some years they were formulated, for example, as $[Fe(COH)_2(CO)_2]$. Nevertheless, standard chemical tests gave no sign of any OH group in the molecule, nor, after the introduction of infrared spectroscopy, were any OH bands found. As Hieber said in the 1930's, these substances behaved as if the hydrogen had entered the nucleus of the metal. Now we know that the hydrogen is directly attached to the metal, and numerous other metal carbonyl hydrides have been discovered, but many are still ill defined. However, some are very important as intermediates in the catalytic addition of carbon monoxide and hydrogen to olefins, an industrial process for the production of long-chain alcohols which are used in the plastics industry.

The modern phase of this subject was opened by accidental discovery of bis(cyclopentadienyl)hydridorhenium in 1955 (*6*). In this substance the cyclopentadienyl anion takes the part of the ligand L. This hydride, like Weichselfelder's hydrides and the carbonyl hydrides, has carbon as ligand atoms in the ligand L, but differs in being thermally stable and well defined. It was discovered when nuclear-magnetic-resonance spectrometers were becoming available as commercial instruments, and the examination of this compound was most important for the development of hydride chemistry. It was found that the resonance of the hydrogen nucleus attached to a transition metal shows an enormous positive chemical shift (τ value) in the nuclear-magnetic-resonance spectrum, as compared with hydrogen attached to main-group elements of the periodic table. This allowed the detection of a number of unstable transition-metal hydrides, which are formed in solution but cannot be isolated. Thus, the addition of potassium cyanide to cobaltous chloride

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in water, long known to give a strongly reducing solution, was now shown by nuclear-magnetic-resonance spectroscopy to contain a substance having hydrogen attached to cobalt. The presence of $[CoH(CN)_5]^{3-}$ was then inferred, but a salt has only recently been isolated (*7*). When this solution is formed in the presence of gaseous hydrogen, $K_3[CoH(CN)_5]$ is formed in rather high concentration, and this compound is a homogenous hydrogenation catalyst for the conversion of alkynes to alkenes. The substance once thought to be potassium rhenide (KRe) in aqueous solution was also shown to have hydrogen attached to the metal.

The final phase was the discovery of hydride complexes with no carbon attached to the transition metal—again an accidental discovery, this time in my own laboratory. The first such complex was a substance, *trans*-$[PtHCl(PEt_3)_2]$ (*8*), so remarkably stable that it can be sublimed in a vacuum. It will dissolve in aqueous ammonia open to the air without oxidation, and the solution can be evaporated on a steam bath, the original hydride being left. The large chemical shift of the unique hydrogen occurs at 26.9 τ, and in the infrared spectrum there is a very strong sharp band at wave number 2183 cm^{-1}, due to the Pt-H stretching vibration.

In the last decade many transition-metal hydride complexes of all levels of stability have been obtained. In general, they have the formula $[MH_xL_y]$, as defined above, and are diamagnetic, and the number and character of the ligands L is such that the metal atom tends to approach the effective atomic number of the next inert gas, or to have two electrons less than the number required by the effective atomic number rule. The first definite examples of paramagnetic hydrides, all three isomers of $[OsHCl_2(PBu^n_2Ph)_3]$, were found only recently (*9*). They have one electron less than the required number.

Apart from hydride complexes of the type $[MH_xL_y]$, there are two complex hydrides, K_2ReH_9 and K_2TcH_9, analogous to the main-group types—for example, $LiAlH_4$.

The crystal structure of K_2ReH_9 has been determined by x-ray and neutron diffraction studies, and the anion structure is shown in Fig. 1. The nine hydrogen atoms are about 1.68 angstroms from the rhenium atom, a reasonable distance for a covalent single bond, and since the rhenium atom must form nine σ-bonds, all its 5*d*-, 6*s*-, and 6*p*-orbitals must be used in σ-bonding.

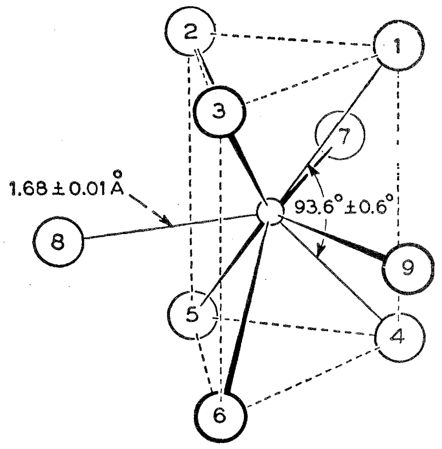

Fig. 1. Arrangement of the hydrogen atoms in $[ReH_9]^{--}$. Atoms 1 to 6 are at the corners of a trigonal prism; atoms 7 to 9 stand out from the center of each prism face. [From S. C. Abrahams, A. P. Ginsberg, K. Knox, *J. Amer. Chem. Soc.* **3**, 558 (1964), reproduced with permission.]

No analogous complex hydrides—for example $K[OsH_9]$—have yet been identified, although analogous hydrides of molybdenum and tungsten may exist (*10*).

The salt K_2ReH_9, stable in alkaline aqueous solution, slowly exchanges hydrogen for deuterium (half-life, 7.8 days at 25°C) in 15-percent KOD-D_2O. The hydrogen atoms behave as if they were all equivalent, and the τ value of 19.1 is among the lower values observed for transition-metal hydride complexes.

Types of Complexes

Table 1 shows the main types of compound now known. A list of individual complexes would occupy many pages. The types are arranged under each metal in periodic-table sequence. It appears that carbonyl and cyclopentadienyl types predominate, but this is really not the case; the formulas listed usually represent only one compound, whereas the general formulas given for the tertiary phosphine types often represent numerous individual compounds, some with as many as three geometrical isomers.

In $[MH_xL_y]$, L is most commonly carbon monoxide, cyclopentadienyl anion, and tertiary phosphines, but halide and similar ions also occur with these, especially in the phosphine and phosphine-carbonyl complexes. The pattern of types is very clear. The carbonyl and cyclopentadienyl types occur to the left and at the top of the transition-metal series, the phosphine and the arsine and halide types, to the bottom and right.

The few types of ligands L involved is at first glance surprising, but had it been possible for more ligands to stabilize the M–H bond, hydrido-complexes would have been known long ago. When the transition-metal complexes containing the common ligands are reduced in aqueous solution, the metal is usually then present in some low oxidation state without hydrogen attached, or it is deposited. Ligands with high ligand field strengths stabilize the hydride species best. Only those with carbon or phosphorus as ligand atoms are really effective; then ligand effectiveness falls off, in tertiary arsines, organic sulfides, amines, oxyacid anions, and halide ions, roughly in that order.

The hydride complexes are usually obtained by reduction or protonation of suitable metal complexes. All the positively charged species listed in Table 1 were obtained by protonation, usually in very strong acid:

$$[Fe(C_5H_5)_2] + H^+ \rightleftharpoons [FeH(C_5H_5)_2]^+ \qquad (1)$$

They were detected, by nuclear-magnetic-resonance spectroscopy, in the acid solutions but were not isolated.

The cations $[ReH_2(C_5H_5)_2]^+$ and $[WH_3(C_5H_5)_2]^+$ are exceptions and are formed in dilute acid. The rhenium complex $[ReH(C_5H_5)_2]$ has almost the same basic strength as ammonia in dioxane solution, but it is not soluble in water. The complex $[TaH_3(C_5H_5)_2]$, having no nonbonding electron pair on the metal, is not basic.

The carbonyl and cyclopentadienyl carbonyl hydrides are usually obtained by hydrolysis of their salts with water or dilute acid:

$$Li[Mo(CO)_3(C_5H_5)] + CH_3COOH \rightarrow [MoH(CO)_3(C_5H_5)] + CH_3COOLi \qquad (2)$$

The salts are obtained by reduction of a carbonyl complex either by treatment with alcoholic potassium hydroxide,

$$[Fe(CO)_5] + 3OH^- \rightarrow [FeH(CO)_4]^- + CO_3^{--} + H_2O, \qquad (3)$$

or directly by reduction with alkali metal or amalgam in a suitable solvent. Special methods are common, especially for the iron series of polynuclear hydrides, where diamines are used to cause "valency disproportion":

$$4[Fe_3(CO)_{12}] + 9\,\mathrm{en} \rightarrow 3[Fe(en)_3][Fe_3(CO)_{11}] + 15CO \qquad (4)$$

In the cyclopentadienyl series, reactions such as

$$LiC_5H_5 + [Mo(CO)_6] \rightarrow Li[Mo(CO)_3(C_5H_5)] + 3CO \qquad (5)$$

are useful.

Direct reduction of the carbonyls by hydrogen under pressure is also possible and produces the hydride directly:

$$[Co_2(CO)_8] + H_2 \rightleftharpoons 2[CoH(CO)_4] \qquad (6)$$

Bis(cyclopentadienyl)hydrides are obtained by the reaction of sodium cyclopentadienide on metal halide in the presence of sodium borohydride:

$$WCl_6 \xrightarrow[NaBH_4]{NaC_5H_5} [WH_2(C_5H_5)_2] \qquad (7)$$

The tertiary phosphine hydrides and halide hydrides result when the complexes of the metal halide with the phosphine are reduced. A number of reducing agents have been used. Lithium aluminum hydride is a general reducing agent, but not usually the best. Hydrazine hydrate and boiling alcoholic potassium hydroxide are very good in special cases—the former, particularly for producing platinum hydride complexes,

$$cis\text{-}[PtCl_2(PR_3)_2] + 2N_2H_4 \rightarrow trans\text{-}[PtHCl(PR_3)_2] + N_2 + NH_4Cl + NH_3, \qquad (8)$$

and the latter especially for producing iridium complexes,

$$[IrCl_3(PR_3)_3] + C_2H_5OH + KOH \rightarrow [IrHCl_2(PR_3)_3] + KCl + CH_3CHO \qquad (9)$$

In reaction 9 a second or third chloride ion can be replaced by, respectively, 2 or 3 moles of KOH, and the reaction is assisted by use of the higher-boiling 2-methoxyethanol. In the ruthenium and osmium series of complexes, alcoholic potassium hydroxide inserts carbon monoxide together with hydrogen, both from the alcohol:

$$[Ru_2Cl_3(PR_3)_6]Cl + 2RCH_2OH + KOH \rightarrow 2[RuHCl(CO)(PR_3)_3] + 2RH + 2KCl + 2H_2O \qquad (10)$$

An interesting method involves the addition of hydrogen gas or hydrogen halide to a complex of the metal in a low oxidation state:

$$[PtHCl(PEt_3)_2] + HCl \xrightarrow{Et_2O} [PtH_2Cl_2(PEt_3)_2] \qquad (11)$$

This type of reaction, now known as oxidative addition, is especially common among d^8 complexes. The addition of hydrogen gas to the planar

Table 1. Types of hydride complexes formed by transition metals.

Groups IV and V	Group VI	Group VII	Group VIIIa	Group VIIIb	Group VIIIc and I
Titanium $TiHCl_3$ $[\{TiH(C_5H_5)_2\}_2]$† Vanadium $[VH(CO)_6]$	Chromium $[CrH(CO)_5]^-$ $[Cr_2H(CO)_{10}]^-$ $[Cr_2H(CO)_6(OH)_3]^{--}$ ‡ $[CrH(CO)_3Ar]^+$ § $Li_3[Cr_2H_3Ph_6]3Et_2O$ $Li_3[CrHPh_5]3Et_2O$	Manganese $[MnH(CO)_5]$ $[Mn_2H_2(CO)_9]$ $[Mn_2H(CO)_9]^-$ $[Mn_3H_3(CO)_{12}]$ $[MnH(CO)_4(PR_3)]$ ‖ $[Mn_2H(CO)_9(PR_3)]$ $[MnH(NO)_2(PPh_3)_2]$ $[C_5H_5)FeMn(CO)_7H]^+$ $[Mn_3H(CO)_{10}(BH_2)_2]$	Iron $[FeH_2(CO)_4]$ $[FeH(CO)_4]^-$ $[Fe_3H(CO)_{11}]^-$ * $[FeH(C_5H_5)_2]^+$ $[FeH_xX_{(2-x)}(diphos)_2]$ ¶ $[FeH(CO)_yY_z]^+$ ** $[FeH(CO)_2(C_5H_5)]$ $[\{Fe(CO)_2(C_5H_5)\}_2H]^+$	Cobalt $[CoH(CO)_4]$ $[CoH\{C_2H_4(PPh_2)_2\}_2]$ $[CoH(CO)_3(PR_3)]$ $[CoH(CN)_5]^-$ $[CoH(PF_3)_4]$ $[CoH(CO)(PF_3)_3]$ $[CoH(dmg)_2B]$†† $[CoH_2\{C_2H_4(PPh_2)_2\}_2]^+$ $[CoH(N_2)(PPh_3)_3]$ $[CoH_3(PPh_3)_3]$	Nickel $[Ni_4H(CO)_9]^-$ * $[NiHCl(PPr_3)_2]$ Copper CuH(solvent)
Zirconium $[ZrH_2(C_5H_5)_2]_2$ $[ZrH(BH_4)(C_5H_5)_2]$ Niobium	Molybdenum $[Mo_2H(CO)_{10}]^-$ $[Mo_2H(CO)_6(OH)_3]^{--}$ $[Mo_2H_3(CO)_6(OH)_3]$‡ $[MoH_2(C_5H_5)_2]$ $[MoH(CO)_3(C_5H_5)]$ $[\{Mo(CO)_3(C_5H_5)\}_2H]^+$ $[MoW(CO)_6(C_5H_5)_2H]^+$ $[\{Mo(CO)_2(PMe_2)(C_5H_5)\}_2H]$	Technetium $[TcH(CO)_5]$ K_2TcH_9	Ruthenium $[Ru_4H_2(CO)_{13}]$ $[RuH(C_5H_5)_2]^+$ $[RuH_xX_{(2-x)}(diphos)_2]$ $[RuHCl(CO)(PR_3)_3]$ $[RuH(CO)_2(C_5H_5)]$ $[\{Ru(CO)_2(C_5H_5)\}_2H]^+$ $[RuHCl(PPh_3)_3]$	Rhodium $[RhH(CO)_4]$ $[RhH_xX_{(3-x)}(QR_3)_3]$ $[RhHCO(PPh_3)_3]$ $[RhH(NH_3)_5]^{++}$ $[RhHCl\ trien]^+$ ‡‡ $[RhH(PF_3)_4]$	Palladium $[PdHCl(PEt_3)_2]$
Hafnium Tantalum $[TaH_3(C_5H_5)_2]$	Tungsten $[WH(CO)_5]^-$ $[W_2H(CO)_{10}]^-$ $[W_2H_3(CO)_6(OH)_3]$‡ $[WH_2(C_5H_5)_2]$ $[WH_3(C_5H_5)_2]^+$ $[WH(CO)_3(C_5H_5)]$ $[WH_2(CO)_2(C_5H_5)]^+$ $[\{W(CO)_3(C_5H_5)\}_2H]^+$	Rhenium $[ReH(CO)_5]$ $[Re_2H(CO)_8O_2]^-$ $[Re_3H_3(CO)_{12}]$ $[ReH(C_5H_5)_2]$ $[ReH_2(C_5H_5)_2]^+$ K_2ReH_9 $[ReH_5(PR_3)_3]$ $[ReH_7(PR_3)_2]$*** $[ReH_2Cl(PR_3)_4]$	Osmium $[OsH_2(CO)_4]$ $[OsH_xH_{(2-x)}(diphos)_2]$ $[OsHCl_2(PR_3)_3]$ $[OsHCl_3(PR_3)_2]$ $[OsHCl(CO)(QR_3)_3]$ ‖‖	Iridium $[IrH(CO)_4]$ $[Ir_4H(CO)_{10}]^-$ $[IrH_xX_{(3-x)}(QR_3)_3]$ $[IrH_xX_{(3-x)}(CO)(QR_3)_2]$ $[IrH(CO)(PPh_3)_3]$ $[Ir_2H_2X_4DE]$¶¶ $[IrH(PF_3)_4]$ $[IrH_3(PR_3)_2]$	Platinum *trans*-$[PtHX(QR_3)_2]$§§ *trans*-$[Pt_2H_2(PPh_2)_2(PEt_3)_2]$ $[PtH_2Cl_2(PEt_3)_2]$ $[PtH(PPh_3)_3]^+$

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* Other, similar polynuclear complexes are known. †C_5H_5 = cyclopentadienyl. ‡Other, similar polynuclear carbonyl hydrides, their anions and derived hydroxy, alkoxy, and similar complexes have been reported. §Ar = aromatic molecule (for example, C_6H_6 and $CH_3C_6H_4Cl$). ‖R = alkyl or aryl group; in PR_3 the R groups need not all be the same. ¶X = halide or other monovalent acid radical; diphos = diphosphine (for example, $R_2PCH_2CH_2PR_2$ and o-$C_6H_4(PEt_2)_2$. **Y = tertiary phosphine or arsine, or carbon monoxide; $y = 3$ or 4, $z = 2$ or 1, respectively. ††dmg = dimethylglyoxime; B = pyridine or triphenylphosphine. ‡‡Trien = triethylenetetramine; other, similar ammine hydrides are known. §§A great number of very stable compounds of this type and a few related compounds are known. ‖‖Q = P or As. ¶¶D = $(CO)_2$, E = $(PEt_3)_2$ or A = E = cyclo-octa-1,5-diene. ***Other derivatives of the general formula $Re_xH_y(PR_3)_z$ (x = 1 or 2) have been reported.

$[IrClCO(PPh_3)_2]$ to give octahedral iridium(III) complexes has been much studied, and the reaction

$$[IrCl(CO)(PPh_3)_2] + H_2 \rightarrow [IrH_2ClCO(PPh_3)_2] \qquad (12)$$

is an oxidation by hydrogen. There are other preparative methods, but reactions 1 to 3 and 6 to 12 are the most common.

General Properties

Hydride complexes are generally colorless solids, but some, especially among the carbonyl hydrides, are colored, and a few, such as $[MnH(CO)_5]$, $[FeH_2(CO)_4]$, $[CoH(CO)_4]$, and the $[MH(PF_3)_4]$ type, are volatile liquids. The cobalt and iron carbonyl hydrides are very volatile, giving off poisonous, evil-smelling vapors.

The thermal stabilities of the molecular hydrides derived from the elements of the main groups of the periodic table fall markedly as one proceeds from the lighter to the heavier elements, as in the familiar series CH_4, SiH_4, GeH_4, SnH_4, and PbH_4. In contrast, the heavier transition metals generally give the more stable hydride complexes, with the possible exception of the purely carbonyl hydrides. This exception may be caused by the very much greater stability of the polynuclear carbonyls of the heavier transition metals, which are products of the decomposition, rather than by the inherent instability of the bond between hydrogen and the heavier transition metals, in their carbonyl hydrides. In all other series, however, the heavier transition metals give the more stable hydrides. Thus the nickel compound $[NiHCl(PPr_3)_2]$ has been detected spectroscopically only in solution. The solid palladium compound $[PdHCl(PEt_3)_2]$ has been isolated, but is very unstable, in marked contrast to its very stable platinum analog, described above.

Generally, of the hydrides listed in Table 1, those to the top and left of the table oxidize readily in air and may be sensitive to moisture, and those at bottom right tend to have relatively high thermal, oxidative, and hydrolytic stability. The carbonyl hydrides tend to be the most sensitive to temperature and oxidation, but the substitution of triphenyl phosphine for carbon monoxide increases stability markedly. Thus $[CoH(CO)_4]$, which is very volatile and decomposes, with loss of hydrogen, at temperatures above about −20°C, has a substitution product, $[CoH(CO)_3(PPh_3)]$, which is stable up to +20°C. This increase in stability may be associated with the higher electron density on the metal atom, because the more electronegative phosphine in $[CoH(CO)_3\{P(OPh)_3\}]$ causes decomposition to start at about 0°C.

Hydride complexes are generally too sensitive to oxidation to be manipulated in the presence of air, and they are handled in a closed system under nitrogen or argon. However, the hydride complexes of osmium, iridium, and platinum, which contain monotertiary phosphines, halogen, and sometimes one molecule of carbon monoxide, are especially stable; they do not oxidize in air, and can be manipulated in open vessels. Compounds of type $[MH(PF_3)_4]$ (where M = cobalt, rhodium, or iridium) also have good thermal, hydrolytic, and oxidative stability, in marked contrast to their carbonyl analogs.

The nature of the hydrogen in the transition-metal hydride complexes varies considerably. In those which contain two or more carbon monoxide molecules it tends to be protic; the most strongly acidic is $[CoH(CO)_4]$, said to be as strongly acid as nitric acid in methanol solution. But generally the acid strengths are very low; thus $[CoH(CO)_3(PPh_3)]$ has an acid dissociation constant of 1.09×10^{-7}. The alkali metal salts are all hydrolytically unstable in water, but stable insoluble salts are produced through combination with large organic or complex cations such as $[Fe(phen)_3]^{++}$.

As mentioned above, both $[WH_2(C_5H_5)_2]$ and $[ReH(C_5H_5)_2]$ are monoacid bases, the proton from solution being attached to an electron pair on the metal. This pair is also available for other strong electron acceptors, such as boron trifluoride in the compound $[WH_2(BF_3)(C_5H_5)_2]$.

The phosphine, monocarbonyl phosphine, and related hydride complexes are neutral, and the hydrogen takes one place, as a halide ion would, in the coordination shell. X-ray crystal structures, which do not show the hydrogen, support this statement. They also show that the bond in the *trans* position to the hydrogen is slightly longer than other, similar bonds in the molecule, and that the angle between the M–H bond and the bonds to the *cis* ligands is rather smaller than that required for the regular coordination polyhedron.

The characteristic hydride resonances in the nuclear-magnetic-resonance spectra occur at τ values of 11 to 42, the carbonyl, arene, and cyclopentadienyl hydrides tending to have the lower values. In binuclear species, high τ values result when the hydrogen is associated with both metal atoms—for example, for $[\{Co(Co)_3(C_5H_5)\}_2H]^+$, $\tau = 30.99$; for $[MoH(CO)_3(C_5H_5)]$, $\tau = 15.52$. Nevertheless the highest value recorded ($\tau = 41.2$) is for the mononuclear complex *trans*-$[FeHCl\{o\text{-}C_6H_4(PEt_2)_2\}_2]$.

The infrared spectra of the hydride complexes show strong bands due to the M–H stretching and bending modes of vibration, but in the carbonyl hydrides the bands are often difficult to identify. The stretching frequencies cover the wave-number range 1700 to 2250 cm^{-1}, and the bending modes occur around 660 to 850 cm^{-1}. There is no obvious correlation between the M–H frequencies, the τ values, and the protonic or hydridic nature of the hydrogen.

Hydrogen is so light relative to the mass of a transition-metal ion that the stretching frequencies are a useful indication of relative M–H bond strengths, provided that only one hydrogen atom is attached to the metal and that other vibration frequencies of the same order, which could couple with it, are absent. The stretching frequencies show that the strength of binding depends very much on the character of other ligands in the complex, especially on that of the ligand *trans* to hydrogen; the greater the *trans* effect of the ligand the weaker the M–H bond and the lower the M–H stretching frequency (see Table 2, where ligands X are listed in order of increasing *trans* effect).

The hydrogen atom itself has a profound effect on the ligand in the *trans* position. Thus in the reaction

$$\textit{trans}\text{-}[PtXCl(PEt_3)_2] + py \rightleftharpoons [PtXpy(PEt_3)_2]^+ + Cl^- \qquad (13)$$

equilibrium is attained 10^5 times faster when X = H than when X = Cl. This labilizing effect of hydrogen is used to catalyze sluggish substitution reactions, under reducing conditions. A transient unstable hydride in low concentration is formed, and the substitution occurs in it. Thus the substitution of chloride ion by nitrogenous ligands in rhodium(III) complexes,

$$[RhCl_3py_3] \xrightarrow[-\ HCl]{+\ H_2} [RhHCl_2py_3] \xrightarrow[-\ H^-]{+\ py} [RhCl_2py_4]^+, \qquad (14)$$

is greatly catalyzed by alcohol, hypophosphorous acid, and hydrogen gas—all believed to act as hydride donors (*11*).

Chemical Reactions

Most of the hydride complexes undergo trivial reactions of the sort expected, in the case of halogen and halogen acids, to give halide complexes together with hydrogen halide and hydrogen, respectively. Many hydride complexes are also chlorinated by highly chlorinated solvents:

$$[PtHCl(PEt_3)_2] + CCl_4 \rightarrow [PtCl_2(PEt_3)_2] + CHCl_3 \quad (15)$$

Condensation, with elimination of hydrogen, is common, especially in the case of the carbonyl hydrides, where the hydrogen tends to be very labile and is reversibly lost:

$$2[MnH(CO)_5] \xrightleftharpoons[200°/250\ atm]{Heat} [Mn_2(CO)_{10}] + H_2 \quad (16)$$

Although manganese carbonyl hydride must be heated, $[CoH(CO)_4]$ starts to decompose at temperature below $-20°C$, and $[FeH(CO)_2(C_5H_5)]$ is so unstable that the acidification of a solution of $Na[Fe(CO)_2(C_5H_5)]$ leads directly to formation of the dimer:

$$2[Fe(CO)_2(C_5H_5)]^- + 2H^+ \rightarrow [Fe_2(CO)_4(C_5H_5)_2] + H_2 \quad (17)$$

The hydride is obtained by sodium borohydride reduction of $[FeI(CO)_2(C_5H_5)]$ in tetrahydrofuran. Hydrogen elimination seldom occurs from the non-carbonyl hydrides, but it will occur between transition-metal hydride complexes and hydrides of main-group elements (*12*):

$$trans\text{-}[PtHCl(PMe_2Ph)_2] + MePh_2SiH \rightarrow trans\text{-}[PtCl(SiMePh_2)(PMe_2Ph)_2] + H_2 \quad (18)$$

$$GeH_4 + 2[MnH(CO)_5] \rightarrow [(CO)_5Mn\text{-}GeH_2\text{-}Mn(CO)_5] + 2H_2 \quad (19)$$

The halides of metals which form very stable organometallic compounds sometimes react with transition-metal hydrides to form stable metal-to-metal bonds:

$$2[RhHCl_2(PR_3)_3] + HgCl_2 \rightarrow [(PR_3)_3Cl_2Rh\text{-}Hg\text{-}RhCl_2(PR_3)_3] + 2HCl \quad (20)$$

$$2[CoH(CO)_4] + HgCl_2 \rightarrow [(CO)_4Co\text{-}Hg\text{-}Co(CO)_4] + 2HCl \quad (21)$$

However, such carbonyl compounds are more readily obtained through the use of the sodium salt, as, for example, in the reaction

$$Bu_2SnCl_2 + 2Na[Co(CO)_4] \rightarrow [Bu_2Sn\{Co(CO)_4\}_2] + 2NaCl \quad (22)$$

Table 2. Influence of the ligands (X) in *trans*-$[PtHX(PEt_3)_2]$ on the Pt-H bond as shown by its stretching frequency [ν(Pt-H) cm^{-1}] in hexane.

X	NO_3	Cl	Br	I	NO_2	SCN	CN
ν(Pt-H)	2242	2183	2178	2156	2150	2112	2041

The most important reactions of the transition-metal hydrides are (i) insertion reactions, where olefins and the like are inserted between the hydrogen and the metal, and (ii) the corresponding eliminations. These two reactions, in succession, lead to olefin isomerization, which becomes catalytic if the hydride species is formed only transiently, and then is important for the petrochemicals industry.

Most hydride complexes undergo insertion reactions at temperatures and pressures that vary according to the labilities of the hydrogen atoms in the complexes. At room temperature and pressure the very labile $[CoH(CO)_4]$ reacts with olefins to form unstable organic derivatives,

$$RCH{=}CH_2 + [CoH(CO)_4] \rightarrow [RCH(CH_3)Co(CO)_4], \quad (23)$$

whereas the very stable platinum(II) complexes need higher temperatures and pressures:

$$trans\text{-}[PtHCl(PEt_3)_2] + C_2H_4 \xrightarrow[80\ atm]{80°} trans\text{-}[Pt(CH_2CH_3)Cl(PEt_3)_2] \quad (24)$$

This latter reaction is reversed by heating the ethyl complex in a vacuum, and even at room temperature the ethyl complex reacts in benzene with hydrogen to regenerate the hydride:

$$trans\text{-}[Pt(CH_2CH_3)Cl(PEt_3)_2] + H_2 \rightarrow trans\text{-}[PtHCl(PEt_3)_2] + C_2H_6 \quad (25)$$

Perfluoro-olefins undergo the same sort of insertion reactions, giving the relatively very stable highly fluorinated alkyl complexes.

The hydride complexes that are of interest as catalysts are those that have stabilities within rather narrow limits. If the hydride complex is too unstable it will not be formed, and if it is too stable it will not undergo subsequent reaction with organic substrates. Nevertheless, a surprising number of useful reactions are known in which a transient transition-metal hydride complex acts as a catalyst for the hydrogenation and isomeration of olefins (*13*).

The catalytic hydride species is formed in hydrogenation systems by three main types of reaction. Its presence is usually inferred from kinetic studies, although it can be isolated in some cases. The three types of reaction are as follows:

1) Heterolytic splitting of H_2,

$$[RuCl_6]^{3-} + H_2 \rightarrow [RuHCl_5]^{3-} + H^+ + Cl^- \quad (26)$$

$$Cu^{++} + H_2 \rightarrow CuH^+ + H^+, \quad (27)$$

where no change in oxidation state of the metal occurs.

2) Homolytic splitting of hydrogen,

$$2[Co(CN)_5]^{3-} + H_2 \rightarrow 2[CoH(CN)_5]^{3-} \quad (28)$$

$$2Ag^+ + H_2 \rightarrow 2AgH^+, \quad (29)$$

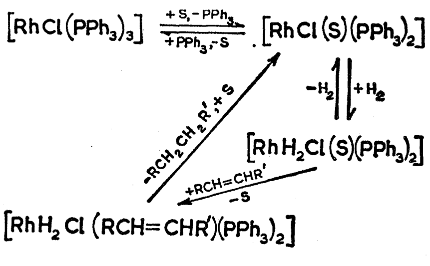
where the oxidation state of the metal is increased by one unit.

3) Addition of H_2 to form a hydride,

$$[IrCl(CO)(PPh_3)_2] + H_2 \rightarrow [IrH_2Cl(CO)(PPh_3)_2], \quad (30)$$

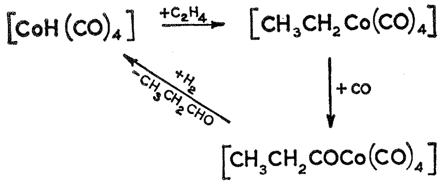
where the oxidation state of the metal is increased by two units.

The hydride species so formed act as transient intermediates in reductions or hydrogenations, and are particularly effective if the organic substrate can easily enter the coordination sphere of the metal. Thus, one of the most active hydrogenation catalysts known is the complex $[RhCl(PPh_3)_3]$. This dissociates in solvents, such as alcohol, and loses one molecule of triphenylphosphine, thus freeing one coordination space to take up an unsaturated organic substance. This complex also reacts with hydrogen to form a hydride, in the manner of reaction 30. Thus, olefin and hydrogen are brought together and react homogeneously and very rapidly even at room temperature, predominantly as follows (*14*):



(S = solvent). Groups R and R′ (R = R′ = H, alkyl or aryl) exert powerful steric influences, and *trans*-stilbene (R = R′ = Ph) hydrogenates very slowly in contrast to cyclohexene and terminal olefins. Alkynes are also hydrogenated.

In carbonyl hydrides the olefin insertion is followed by carbon monoxide insertion and hydrogen cleavage, when those gases are present—processes that lead to a cyclic reaction in which olefins are converted to ketones or aldehydes, as follows:



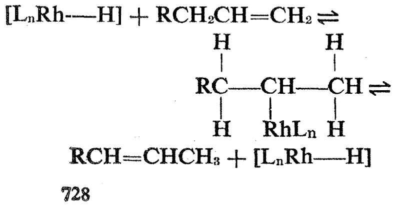
The organic carbonyl can now insert itself; then cleavage leads to the production of an alcohol:

$$[CoH(CO)_4] \xrightleftharpoons[+\ H_2,\ -RCH_2OH]{+\ RCHO} [RCH(OH)Co(CO)_4] \qquad (31)$$

These reactions occur simultaneously. The olefin insertion reaction occurs at room temperature with cobalt carbonyl hydride, and non-terminal olefins ultimately give ketones. However, a cobalt salt with hydrogen, carbon monoxide, and the olefin at higher temperatures and pressures produces the carbonyl hydride moiety on the surface of the metal, formed by reduction of the salt. Now, both terminal and non-terminal olefins react to form mainly aldehydes and primary alcohols. This reaction is known as the Oxo- or hydroformylation reaction and is used in the manufacture of long-chain alcohols for the plastics industry. The overall reaction is

$$C_nH_{(2n+1)}CH{=}CHC_mH_{(2m+1)} \xrightarrow[\text{Cobalt catalyst}]{+CO,\ +2H_2} C_{(n+m+2)}H_{(2n+2m+3)}CH_2OH \qquad (32)$$

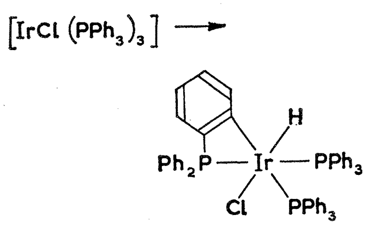
The isomeration of non-terminal olefins which, in reaction 32, leads ultimately to the formation of primary alcohols probably occurs through a hydride intermediate. Many transition-metal compounds in organic solution cause double-bond migration, giving the equilibrium mixture of isomeric olefins. The minute amounts of hydride needed are produced by reaction of the metal complex with solvent, hydrogen, or the olefin. Successive rapid addition and elimination of olefin then occurs, until equilibrium is established. Rhodium trichloride in alcohol is very effective:



$$[L_nRh{-}H] + RCH_2CH{=}CH_2 \rightleftharpoons \begin{array}{ccc} H & & H \\ | & & | \\ RC & {-}CH{-} & CH \\ | & | & | \\ H & RhL_n & H \end{array} \rightleftharpoons RCH{=}CHCH_3 + [L_nRh{-}H] \qquad (33)$$

The ligands L may include solvent, halide ion, and olefin (*15*). The hydrogen may also be transferred from one molecule to another. Some hydrides, especially $[IrH_3(PPh_3)_3]$, decompose formic acid to carbon dioxide and hydrogen in boiling acetic acid solution, and in the presence of an aldehyde produce the alcohol (*16*).

Thus, because hydrogen can so easily become a ligand, transition-metal complexes encourage hydrogen migration even in essentially saturated systems. Indeed, all degrees of interaction of substrates with the metal ion occur, from slight weakening of the bond to hydrogen, as detected by spectroscopic methods and x-ray structure (*17*), to complete severance of hydrogen from its ligand (*18*), as in the reaction



(34)

There is even an example of a reversible reaction of the type of reaction 34 (*19*). In such reactions, when the metal atom inserts itself into a C–H bond, the metal increases both its oxidation number and its coordination number by two units.

The complexes of transition metals in low oxidation states especially have this capacity to take hydrogen from the ligand, solvent, or hydrogen gas, and thus to increase the oxidation number of the metal. Thus the reaction must be one where the metal, which behaves as a nucleophile, attacks the antibonding orbitals on the molecule containing hydrogen. The metal ion has taken the role of electron donor rather than its more usual one of electron acceptor. This capacity of transition-metal ions in low oxidation states to behave as both donors and acceptors is important for the formation of complex compounds of unsaturated and aromatic hydrocarbons, carbon monoxide, and, as has only recently been realized, nitrogen (*20*). It provides a mechanism whereby these substances may be brought into reaction together and with hydrogen.

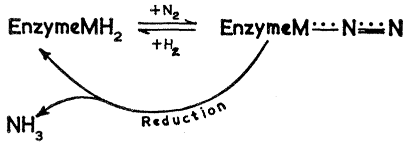
Nitrogen complexes in this context open the intriguing prospect of the catalytic hydrogenation of nitrogen to hydrazine or ammonia under mild conditions. The most interesting nitrogen complex so far found is $[CoH(N_2)(PPh_3)_3]$, which is produced from nitrogen gas by various methods, including the reaction

$$[CoH_3(PPh_3)_3] + N_2 \rightleftharpoons [CoH(N_2)(PPh_3)_3] + H_2, \qquad (35)$$

in alcohol at ordinary temperature and pressure (*21*). In such complexes the nitrogen molecule is held by one end, rather as the N_2 group in diazomethane is bonded to the methylene group.

This is as near as any chemist has come to finding a substance which will take up nitrogen gas in a protic solvent under conditions as mild as one would expect to find in biological systems which "fix" atmospheric nitrogen—that is, which convert atmospheric nitrogen to ammonia, to be metabolized by the fixing organism or its host plant (*22*). Hydrogen is a competitive inhibitor of natural nitrogen fixation, just as it is a competitor with nitrogen for the active site in the cobalt complex discussed above. Thus it seems that the cobalt complex offers a site very similar to that which occurs in the nitrogen-activating enzyme, nitrogenase. The cobalt-nitrogen complex has not yet been reduced to ammonia, but the nitrogen in $[Ru(NH_3)_5N_2]^{++}$ can be reduced (*20*), and such reduction of the nitrogen molecule must occur after it has been taken up by the nitrogenase.

Many chemists think that a transition-metal hydride complex plays an important role in the biological fixation of nitrogen, perhaps as reducing agent (*23*), and, as now seems likely, protects the nitrogen-activating site, which is assumed to be a transition-metal ion in the enzyme. Thus a simple scheme for nitrogen fixation, involving a transition metal (M) hydride complex,



can be formulated but is far from being confirmed (*24*).

This account of hydride complexes is incomplete, but sufficient to show their great scope and unique interest in all fields of chemistry. Nearly all we know of these substances has been discovered in the last 12 years, and there is no sign of slackening in the pace of discovery.

Summary

Hydride complexes of transition metals were virtually unknown 12 years ago, but they have now been found to

lie at the root of many interesting catalytic chemical reactions, some of which were used in industry even before the unique properties of hydride complexes, which formed their basis, had been realized.

This article surveys the history, preparations, important properties, and reactions of hydride complexes, surveys their part in important catalytic industrial processes, and speculates about their possible role in the biological fixation of nitrogen.

References and Notes

1. Ligands are atoms or molecules capable of direct chemical bonding to a metal ion. In [MH_xL_y], H is also a ligand, formally treated as H^-; L represents a great variety of chemical groups, such as chloride ion, the cyclopentadienyl anion, ammonia, triphenylphosphine, and aromatic and unsaturated hydrocarbons. The following abbreviations are used in the article: Bu^n, normal butyl; Et, ethyl; en, ethylenediamine; Me, methyl; Ph, phenyl; phen, *o*-phenanthroline; Pr, propyl; py, pyridine.
2. Because of limitations of space, this summary is necessarily incomplete. For detailed information and all except historical or very recent references, see A. P. Ginsberg, *Transition Metal Chem.* 1, 111 (1965); see also J. Chatt, *Proc. Chem. Soc.* **1962**, 318 (1962), and M. L. H. Green and D. J. Jones, *Advan. Inorg. Nucl. Chem.* **7**, 115 1965).
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22. Since this was written the nitrogen complex, $[Ru(NH_3)_5N_2]^{++}$ has been obtained from $[Ru(NH_3)_5H_2O]^{++}$ and gaseous nitrogen in aqueous solution [D. E. Harrison and H. Taube, *J. Amer. Chem. Soc.* **89**, 5706 (1967)].
23. See, for example, G. W. Parshall, *ibid.* **89**, 1822 (1967).
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Atmospheric and Hydrospheric Evolution on the Primitive Earth

Both secular accretion and biological and geochemical processes have affected earth's volatile envelope.

Preston E. Cloud, Jr.

This discussion focuses on the interactions that necessarily took place between biospheric, atmospheric, lithospheric, and hydrospheric evolution on the primitive earth and perhaps the moon. How can evidence and conjecture about each of these different kinds of evolution limit or illuminate hypotheses about the others, and how can all such lines of thought be integrated to bring us closer to a consistent and plausible model of early terrestrial events?

A salient and long-appreciated aspect of the terrestrial atmosphere is its great depletion in the noble gases, relative to their cosmic abundances (*1*). This seems to require the conclusion that the atmosphere as we know it is of secondary origin. Either the earth originated without a primary atmosphere, or such an atmosphere was mainly lost in a subsequent thermal episode.

Actually, an internal source for our atmosphere as a result of gradual, episodic, or rapid volcanic outgassing and weathering was proposed long before the depletion in noble gases was recognized. The Swedish geologist Högbom (*2*) suggested this in 1894, and his countryman Arrhenius (*3*), in 1896. Later Chamberlin (*4*) recognized a post-accumulational generation of the atmosphere from occluded gases as a necessary consequence of his and Moulton's planetesimal hypothesis for the origin of the earth. Rubey's critical and comprehensive assessment (*5*) of possible sources for the volatiles that comprise the atmosphere and hydrosphere has led to wide acceptance of the concept of accumulation of both from juvenile sources.

As far as the atmosphere is concerned, dispute focuses on the composition and time of origin of the primitive atmosphere and the original proportions and changes in the proportions of O_2, N_2, CO_2, and H in it.

The atmosphere cannot be older than the earth. Hence an outside limit on its time of origin is the time of origin of the earth. Much evidence has been adduced in recent years, based on the ages of meteorites (*6, 7*) and on isotopic composition of terrestrial leads (*7, 8*), to suggest that both meteorites and leads were involved in some kind of homogenization event about 4.6×10^9 years ago (10^9 years is hereafter referred to as an aeon). Small excesses of xenon-129 in some meteorites (*9*) support the inference that this event closely approximates the time of origin of the solar system and hence the approximate time of formation of the earth. Such an interpretation, however attractive and highly probable as it seems, is not the

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The author is professor of geology, University of California, Los Angeles. This article is adapted from a paper presented 27 December 1967 at the New York meeting of the AAAS, as a part of the Lloyd V. Berkner Memorial Symposium of the Section on Astronomy. The last half is also a greatly condensed and evolved version of a 1967 Sigma Xi National Lecture and of a longer paper, "Pre-metazoan evolution and the origins of the Metazoa," in *Evolution and Environment* (Yale University Press, New Haven, in press).