that previous half-times of reaction in 80% Me_2SO were underestimated.[20]

(28) Voltammograms of this couple measured at a different electrode are given elsewhere.[12,23]

(29) E. E. van Tamelen, J. A. Gladysz, and C. R. Brûlet, *J. Am. Chem. Soc.*, **96**, 3020 (1974).

(30) K. Tano and G. N. Schrauzer, *J. Am. Chem. Soc.*, **97**, 5404 (1975).

(31) J. A. Ibers, J. Renaud, and R. H. Holm, results to be submitted for publication.

(32) S. G. Mayhew, D. Petering, G. Palmer, and G. P. Foust, *J. Biol. Chem.*, **244**, 2830 (1969); K. Uyeda and J. C. Rabinowitz, *ibid.*, **246**, 3111 (1971).

(33) G. N. Schrauzer, G. W. Kiefer, K. Tano, and P. A. Doemeny, *J. Am. Chem. Soc.*, **96**, 641 (1974).

(34) Y. Sugiura, K. Ishizu, T. Kimura, and H. Tanaka, *Bioinorg. Chem.*, **4**, 291 (1975).

(35) Y. Sugiura, K. Ishizu, and T. Kimura, *Biochem. Biophys. Res. Commun.*, **60**, 334 (1974).

(36) D. O. Hall, R. Cammack, and K. K. Rao, *Origins Life*, **5**, 310 (1974); D. O. Hall, K. K. Rao, and R. Cammack, *Sci. Prog. (Oxford)*, **62**, 285 (1975).

(37) J. Cardenas, L. E. Mortenson, and D. C. Yoch, *Biochim. Biophys. Acta*, **434**, 244 (1976).

(38) For a discussion of the biosynthesis of Fe–S proteins cf. J. W. Brodrick and J. C. Rabinowitz in "Iron-Sulfur Proteins", Vol. III, W. Lovenberg, Ed., Academic Press, New York, N.Y., 1977, Chapter 4.

Contribution from the Department of Chemistry,
University of Victoria, Victoria, British Columbia, Canada

Formation and Isolation of $FeH_6Mg_4X_4(C_4H_8O)_8$[1]

SIDNEY G. GIBBINS

Reaction of iron(III) chloride with excess hydrogen and phenylmagnesium bromide resulted in 3.5–4.2 mol of hydrogen absorbed/mol of iron. Vapor-phase extraction of the black products with tetrahydrofuran yielded the yellow crystalline solid (YCS) $FeH_6Mg_4X_4(THF)_8$ where X comprised bromide plus chloride. The extreme sensitivity of the nonvolatile solid to air and water necessitated the development of numerous new manipulative methods. Pyrolysis of the YCS yielded 96% of the THF below 160 °C. Hydrogen evolution was significant above 200 °C. Hydrolysis of the compound initially yielded metallic iron along with hydrogen and magnesium halides.

Attempts to isolate and characterize the iron hydride formed by the reaction of excess phenylmagnesium bromide with iron(III) chloride in diethyl ether under an atmosphere of hydrogen have resulted in diverse experimental observations and controversial conclusions. The reaction was first reported in 1926 by Weichselfelder[2] who claimed to have prepared FeH_6. On mixing an ethereal solution of iron(III) chloride with the Grignard under hydrogen, a tan precipitate was rapidly formed and within 10 min it was either consumed or obscured by a black solution from which a viscous black oil later separated. Absorbed hydrogen corresponded to $FeH_{6.1}$. Hydrolysis of the entire mixture yielded hydrogen corresponding to $FeH_{5.8}$. When Ray and Sahai[3] repeated the reaction, a black precipitate formed. The precipitate was washed with diethyl ether and then hydrolyzed. The H/Fe ratio was 3, and magnesium and organic impurities were slight. Haenny and Levi,[4] without the support of experimental data, ascribed the hydrogen absorption to hydrogenation of the phenyl group. Wiberg, in a personal communication to Sarry[5] and also to Tullis,[6] reported that he had prepared black FeH_6. Sarry[5] repeated the synthesis and attempted to wash the product free of excess Grignard with pyridine. While the analysis of the purified black product varied widely, the average composition corresponded to FeH_3. Considerable magnesium and a minimum of 39% unidentified organic matter were also present. Takegami and Fujmaki,[7] interested primarily in catalytic hydrogenation, carried out the reaction under a wide variety of conditions. They postulated formation of $Mg(FeH_4)_2$ on the basis of hydrogen absorption on reaction and evolution on hydrolysis of an aliquot of the crude mixture. No product was isolated. Kost et al.[8] obtained black products which they washed with ether. When the $C_6H_5MgBr/FeCl_3$ reaction ratio was 34, a cream-colored product was isolated which contained H/Mg of 0.2 and no iron. When the reaction ratio was 16, the final black product contained magnesium, iron, and hydrogen in the ratio of 10/1/3, respectively.

A wide variety of experimental approaches resulted in diverse conclusions. Hydrogen consumption on reaction and evolution on hydrolysis varied by more than a factor of 2. A fundamental difficulty was the assumption that valid conclusions could be deduced from incomplete analytical data derived from complex mixtures. Analytical samples were weighed in only one case.[5] A total analysis was performed in no instance.

This writer initiated work on the problem when the field of transition metal hydrides was almost exclusively limited to groups 3B, 4B, and 5B elements and palladium. The problem was significant from both an intrinsic and an applied point of view. Since iron was known to form an endothermic hydride, any stoichiometric binary hydridic product from Weichselfelder's reaction was anomalous. As complex hydrides became known, it appeared that back-bonding ligands were the prerequisite for formation of a stable Fe–H bond. The principal established exception was K_2ReH_9.[9] The possible uses of hydrides as high-energy fuels and as high-density moderators in nuclear reactors were practical reasons for studying the problem. A timely reason for studying the problem is for the information that may be obtained regarding hydrogenation catalysis.

Experimental Section

The extreme oxidative and hydrolytic sensitivity of the hydridic product and the wide range of results obtained by previous investigators dictate that the experimental procedure be described in detail.

Reactants. Iron(III) chloride was prepared from the elements in an all-glass system. It was purified by vacuum sublimation through a series of three bulbs and then collected in a weighing vessel.[10] All weights reported here, except where indicated, were determined to ±0.1 mg. At no time was the iron(III) chloride exposed to oxygen or water.
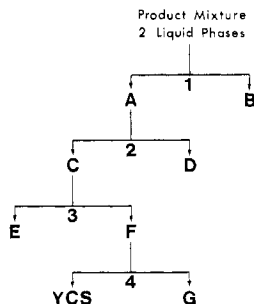
The phenylmagnesium bromide was prepared in the usual manner and then filtered in order to remove metallic magnesium.

The hydrogen used was reported by the manufacturer to contain less than 1 ppm impurity. It was stored in volume-calibrated bulbs equipped with Torricelli-type manometers and was admitted to the reaction vessel via fragile bulb break-seals.

All solvents were dried by sodium benzophenone and then distilled into the vacuum line without exposure to the atmosphere. Diethyl ether and tetrahydrofuran (THF) were dried a second time by condensation in storage vessels sealed to the vacuum line and containing sodium benzophenone. The necessity for this double drying was indicated by the reactivity of the hydridic product.

The Reaction. The hydride formation reactions (Table I) were carried out in a reactor[10] maintained at room temperature except when indicated. The reactor, connected to a standard borosilicate vacuum line via a mercury-protected stopcock, was evacuated to less than 10^{-5} Torr and flamed out to remove adsorbed moisture. The method of

Chart I. Purification Process A

```
            Product Mixture
            2 Liquid Phases
                   |
          |        1        |
          A                 B
          |                 |
          |        2        |
          C                 D
          |                 |
          |        3        |
          E                 F
                   |        |
                   |   4    |
                  YCS       G
```

Chart II. Purification Process B

```
            Product Mixture
             1 Liquid Phase
                   |
          |        1        |
          A                 B
                   |        |
                   |   2    |
                   C        D
                   |
          |        3        |
          E                 F
          |                 |
          |            |    4    |
          |            G    H    I
          |            |
          |        5        |
          J                 K
                   |        |
                   |   6    |
                   L        M
                            |
                   |        7        |
                   N                 O
                   |                 |
                   |            |    8    |
                   |            P        Q
                   R                     |
          |        9        |            |
         YCS                S ───────────┤
                                         T
```

reactant addition is described in ref 10. After formation of the iron(III) chloride diethyl ether solution, hydrogen was admitted and then the system was magnetically stirred overnight. On addition of the Grignard, preparation 4 (Table I) was sufficiently exothermic that cooling was required to maintain it at room temperature. Except for preparation 4, a tan precipitate formed but within 10 min the solution turned black. In preparation 4, the solution rapidly darkened and the precipitate was not observed. The hydrogen consumption was directly related to the stirring rate. The reaction was presumed complete when no additional hydrogen was consumed for a period of several days. This was determined by measuring the pressure of the noncondensable gas after the liquid was cooled to -80 °C overnight.

After termination of the reaction, the products were cooled to -80 °C. The excess hydrogen was passed through a series of traps cooled to -196 °C and then pumped into a calibrated volume. At no subsequent time was hydrogen ever observed to be spontaneously evolved from any product at room temperature. Furthermore, no hydrogen was evolved when the nonvolatile products of preparation 2 were heated to 72 °C.

Purification Operations. Although the problems of product separation and purification were similar in the three reactions, they differed in detail due to the physical state of the reaction mixture. In preparation 4, one homogeneous black liquid phase resulted whereas in the others, two liquid phases formed. The less dense phase was tan-gray and the heavier, approximately 20% of the liquid volume, was a black viscous oil. Solids, both black and white, also separated. Purification process A was applied to the two-phase case and process B to the single phase one. These processes depended upon solubility properties. As a result of the complex system containing concentrated Grignard, benzene, hydridic products, and probably also magnesium halides, biphenyl, colloidal iron, and other as yet unidentified components, solubility anomalies occurred. The relationship between the purification steps and the fractions obtained therefrom is shown in the two flow diagrams labeled Chart I and Chart II. When the text refers to a particular step, e.g., step 1, or a particular fraction, e.g., A, it is designated on the flow diagram by that number or letter.

Purification Process A (Chart I). The reactor was sealed off the vacuum line and onto a large scale filtration apparatus.[11] The less dense phase (B) was decanted and collected in the filtrate receiver (step 1). Ether was condensed back onto the heavier black oil (A) in the reactor and the mixture was warmed to room temperature and was then stirred for several hours. The dark wash solution (D) was then decanted from the black oil (step 2). The cycle was repeated about ten times. At the end of the washing process, the wash liquor (D) possessed a slight straw yellow color and the black oil had solidified to a powdery black solid (C). The solidification process was aided by cooling the mixture to -196 °C. In one reaction, the stirring bar lost its magnetic properties.

The ether-insoluble black solid (C) collected primarily on the filter which was then sealed off from the filtrate receiver and the reactor. A new filter-filtrate receiver[11] was sealed onto the initial filter. Tetrahydrofuran was condensed in the system, and the black products were repeatedly washed and filtered (step 3). The undissolved black components were ferromagnetic (E). The black filtrate (F) was transferred to a two-bulb vapor-phase extractor.[12] After numerous extractions (step 4), a beautiful lemon yellow crystalline solid (YCS) was obtained free of the more "soluble" black contaminate (G). The YCS was then transferred to a sample subdivision apparatus.[13] During process A, the vast quantities of white crystalline solid (WCS) observed in process B were not encountered. This was probably due to the relative quantities of the reactants and the solvent.
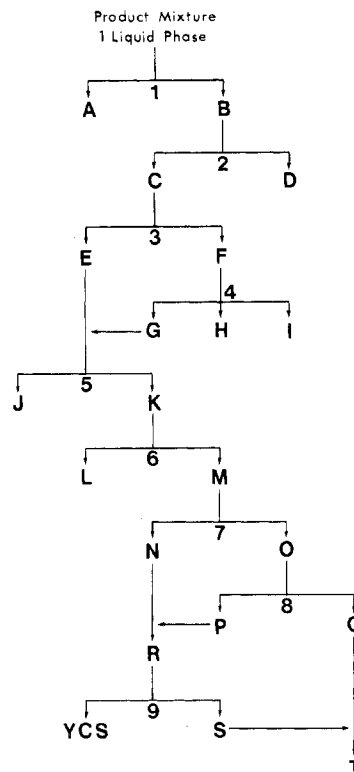
Purification Process B (Chart II). A considerable amount of undissolved WCS (A) was removed from the black ethereal solution, 400–450 mL, by filtration[11] (step 1). On concentration of the filtrate (B) to 250–300 mL, additional WCS was precipitated (D) and was separated by filtration (step 2). The volatile components (F) of the black filtrate (C) were distilled at room temperature into the vacuum line (step 3) where benzene (H) was separated from the ether (G) by passage of the latter through a trap cooled to -80 °C (step 4). The benzene was identified by its vapor pressure and mass and infrared spectra. During the benzene separation operation and in numerous other instances, a sublimable unidentified white crystalline solid (I), probably biphenyl, was observed. The WCS designated herein was not sublimable and was in considerably greater quantity than the sublimable material.

The benzene-free ether (G) was condensed onto the black solid (E) from which it previously had been distilled. The solid slowly dissolved except for some WCS (J) which was removed by filtration (step 5). The filtrate (K) was divided into two parts (1:4) and each was treated in the following manner. After transfer of the etheral solution (K) to a three-ball vapor-phase extractor,[14] the ether was replaced by THF. The following three component types in order of increasing solubility were present: YCS, the more soluble WCS, and the very soluble Grignard black component. On subjecting the mixture to vapor-phase extraction numerous times,[12] all the observable black component and much of the WCS (L) was removed (step 6). The slightly soluble YCS (M), contaminated by WCS, was then treated in the following manner. The impure mixture was washed with approximately 100 mL of THF and then the solution (O) was decanted from the solid (N) into the second bulb (step 7). The THF was evaporated to 25 mL and the WCS-enriched solution (Q) was decanted into the third bulb (step 8). The precipitated YCS (P) was redissolved and combined with fraction (N) in the first bulb to give fraction (R). This process was repeated numerous times and when all the WCS appeared removed, the operation was terminated. To ensure complete WCS removal, the YCS (R) was washed four additional times with 100–150-mL batches of THF (step 9). Each time the entire solution (S) was decanted directly into the final bulb (T) without the intermediate concentration operation. The purified YCS (20–25 g) was then subdivided.[13]

Weighing Transfer Operation. The weighing method[15] for this extremely reactive compound was modified to provide an additional purification operation. To more rapidly transfer the YCS from the

Table I. Reaction Stoichiometry

Prepn[a]	Amt of (C$_2$H$_5$)$_2$O, mL	Amt of FeCl$_3$, mmol	Amt of H$_2$ consumed, mmol	H$_2$:Fe	C$_6$H$_5$MgBr Amt, mL	C$_6$H$_5$MgBr Concn, M	Reaction time, days
2	100	2.12	8.25	3.9	7	3	2.8
3	200	8.78	36.8	4.2	34	3	13
4	200	108.0	374	3.5	500	2	56

[a] The only data available for preparation 1 is that the hydrogen absorbed corresponded to FeH$_{6.1}$ and the hydrogen evolved upon hydrolysis of the entire reaction mixture corresponded to FeH$_{5.9}$.

Table II. YCS Hydrolysis Results

Run	Sample mg	Sample mmol[a]	Amt of H$_2$-HD-D$_2$, mmol	% H$^-$ [b]	Fe[c] mmol	Fe[c] %	Mg[d] mmol	Mg[d] %	Br[d] mmol	Br[d] %	Cl[d] mmol	Cl[d] %
1	371.4	0.3609	2.164	0.5873								
2	196.1	0.1906	1.143	0.5875			0.759	9.41				
3	283.1	0.2752	1.654	0.5889			1.109	9.52	0.950	26.81	0.189	2.36
4	326.8	0.3177					1.269	9.44	1.130	27.63	0.181	1.96
5	236.4	0.2298			0.232	5.48	0.940	9.65				
6	205.4	0.1996			0.200	5.44	0.799	9.45				
7	113.6	0.1104			0.109	5.36	0.447	9.56				

[a] On the basis of Mg$_4$Br$_{3.39}$Cl$_{0.61}$H$_6$Fe(THF)$_8$. [b] On the basis that 50% of the evolved gas was hydrogen. [c] Data for the iron analyses in runs 1 through 4, not included for consideration, were low due to an imperfect analytical scheme. [d] Only the average value for each component is shown.

sample subdivision tube, the THF was increased from 10 to 50 mL. Even though the added THF previously was in contact with YCS, a slight black discoloration always occurred. As the magnetic properties of the dark stream lines indicated colloidal iron, some decomposition occurred and additional purification was in order. A 100-mL bulb was sealed via a constricted 10-mm tube onto bulb 3 of the weighing transfer apparatus. The darkened solution in bulb 2 was concentrated by condensation of the solvent in the new bulb. The final 10 mL of the darkened solution was then poured into the new bulb. The process was repeated and then the new bulb, which contained the nonvolatile products, was sealed off. The weighing transfer operation was then carried out.

YCS Analysis. Analysis was mainly by hydrolysis and pyrolysis. The quantitative recovery of the THF required that the analytical apparatus was grease and stopcock free. The glass apparatus consisted of a reactor, a volatile product collection train, and a Toepler pump followed by a calibrated volume. In the case of pyrolysis, the reactor was a quartz tube. The volatile product collection train consisted of three U tubes in series. Each U tube could be sealed off and each possessed a standard taper joint to which was black waxed a weighed fragile bulb.[15]

YCS Hydrolysis. Hydrolysis was initiated either by condensing a weighed sample of D$_2$O on the YCS followed by warming to room temperature or by breaking fragile bulbs containing each material together at room temperature. The evolved noncondensable gas was measured and mass spectrometrically analyzed for hydrogen and deuterium content. Despite the use of calibrated samples, efforts to precisely determine the H/D ratio using a Perkin-Elmer Hitachi RMU6E mass spectrometer were unsuccessful due to variation in sensitivity of m/e 2 with respect to 3 and 4 from run to run. The precision of the measurement was approximately 4%.

The nonvolatile products were dissolved in dilute nitric or hydrochloric acid. In the first four hydrolyses the iron was homogeneously precipitated and filtered. It was determined using EDTA and a mercury chelate electrode. The filtrate was analyzed for magnesium by titration with EDTA using eriochrome T. Bromide and chloride were determined by silver titration potentiometrically. Approximately 10% of the magnesium coprecipitated with the iron. This was determined by EDTA titration after solution and reprecipitation of the iron. The samples were of sufficient size that frequently two or three aliquots were analyzed for each component. In the last three hydrolyses, iron and magnesium unseparated from one another were determined by atomic absorption spectroscopy.

YCS Pyrolysis. These experiments varied from 8 to 821 h and all were terminated when the temperature reached 780–800 °C. Tetrahydrofuran was continuously condensed in the U tubes and later was transferred to fragile bulbs and weighed. Gas chromatographic, infrared, and mass spectrographic analyses established that THF was the only volatile, condensable product. Hydrogen was periodically

measured and in some cases its evolution at selected temperatures was recorded as a function of time. After termination of the pyrolysis, a weighed quantity of D$_2$O was condensed on the nonvolatile residue and heated. The evolved deuterium was always less than that calculated for conversion of the metallic products to iron(II) hydroxide and magnesium hydroxide. Since subsequent efforts to completely dissolve the nonvolatile residue were unsuccessful, magnesium, iron, and halogen values were low.

Solubility and Derivative Studies. With the ojective of determining separation methods and preparing new solvated compounds, the solubility properties of the reaction products in various solvents were determined using the apparatus and procedures described in ref 16. The black THF-soluble product appeared to be colloidal iron since its dilute solutions scattered light and stream lines were bent in a magnetic field.

Reaction of YCS with tetraethylammonium chloride and also with potassium hexafluorophosphate were carried out in the manner described.[17] Since extensive decomposition occurred in both cases, no derivatives were isolated.

Results

Table I is a resume of the hydride formation reaction conditions. All analytical results were derived from the products of preparation 4. Benzene formation in preparation 4 was 0.37 mol. It was not determined in the other reactions.

The YCS hydrolysis results are compiled in Table II. Although the individual bromide and chloride values varied, the mole ratio of (Br + Cl):Mg was constant. The following results were obtained from multiple titrations

Hydrolysis	% Br	% Cl
3	26.92, 26.70	2.20, 2.51
4	27.50, 27.69, 27.69	2.11, 1.92, 1.87

The first, second, and third bromide values in each row are associated with the corresponding chloride value. In the individual hydrolyses, the standard deviation would be about 0.1% for bromide and 0.2% for chloride. Whether the wide range of the halide results is real or due to difficulty in interpretation of the first end point is unknown. The standard deviations for the other components are shown in Table V.

Hydrolysis 1 was carried out by the addition of the D$_2$O to the YCS at room temperature. Black, ferromagnetic, fibrous particles were blown through the reactor. In places, the fibers formed a spider-like web which stretched across the interior of the tube (20 mm i.d.). The granular black products in D$_2$O at the bottom of the reaction tube developed a gray-green color after heating at 60 °C for 35 min. Of the 2.105-mmol of

Table III. YCS Pyrolysis

Pyrolysis	Sample wt, mg	Heating period, total hours	% THF	% H⁻
1	272.1	8	51.0	0.810
3	405.4	315	55.1	0.647
4[a]	273.2	47	53.2	(0.712)[b]
5[a]	212.4	597	53.8	(0.772)[b]
6	276.9	33	54.3	0.668
7	295.4	821	55.0	0.661

[a] Pirani head present. [b] Mass spectral analysis established that there was an air leak of unknown extent.

Table IV. Tetrahydrofuran Recovery

Pyrolysis	Amt of THF recovered, mg	Heating range, °C	Heating duration,[a] h
3	175.9	25–72	40
	27.9	72–110	114
	11.3	110–163	153
	8.8	163–400	295
5	105.3	25–106	480
	4.5	106–148	576
	4.3	148–800	597

[a] The total time heated below or at the higher temperature cited in the "heating range".

hydrogen–deuterium evolved, 50% was hydrogen. After the volatile components were distilled out, hydrochloric acid was condensed in the reactor which was then heated at 75 °C for 5 h. An additional 0.059 mmol of noncondensable gas was evolved. Surprisingly, 22% of this was deuterium.

In hydrolysis 2, the initial reaction was exothermic. The black nonvolatile products changed to a gray-green color over a period of 52 days at room temperature. After heating of the products at 90–100 °C for 3 days, 1.143 mmol of hydrogen–deuterium was collected. Forty-eight percent of this was hydrogen. Two days of heating at 100 °C and 3 days at 270 °C did not produce any additional hydrogen–deuterium.

Hydrolysis 3 was carried out by condensing the D_2O on the YCS at −196 °C and then permitting the mixture to warm to room temperature at a rate determined by air conduction. After the mixture remained at room temperature for 2 days, 1.547 mmol of hydrogen–deuterium (48.5% hydrogen) was collected. The products were then heated at 200 °C for 14 days and an additional 0.107 mmol of hydrogen was collected. The H/D ratio was not determined.

Table III is an abbreviated compilation of the pyrolysis results. Tetrahydrofuran recovery as a function of heating range in pyrolyses 3 and 5 is shown in Table IV. Two to four percent, depending on the heating duration, of the hydrogen was evolved below 150 °C. In pyrolysis 6, only 0.6% of the hydrogen was evolved when the sample was heated at 95 °C for 6.5 h. Hydrogen evolution was rapid at 200 °C. In all cases, more than 95% of the hydrogen was evolved below 350 °C and 99% below 500 °C. Above 500 °C a metallic mirror, probably magnesium, condensed on the cooler portions of the reactor tube. The solid product which remained in the reaction zone was black and ferromagnetic.

The solubility of the YCS in THF, estimated in the weighing transfer process, was approximately 0.002 M. From THF, the YCS was crystallized as hexagonal platelets some of which were over 3 mm in size.

Treatment of the YCS with dioxane resulted in solution and slight (1%) hydrogen evolution. On evaporation of the solvent, yellow octahedrally shaped crystals 1 mm in size were obtained. Treatment of a second sample of YCS with 1,2-dimethoxyethane initially resulted in complete solution in 10 mL. Overnight, decomposition to metallic iron and hydrogen oc-

Table V. $FeH_6Mg_4Br_{3.39}Cl_{0.61}(THF)_8$

Component	% obsd	% calcd
Mg	9.51 ± 0.09[a]	9.45
Br	27.2	26.37
Cl	2.2	2.09
H⁻	0.588 ± 0.001[a]	0.588
Fe	5.43 ± 0.06[a]	5.43
THF	55.1	56.07

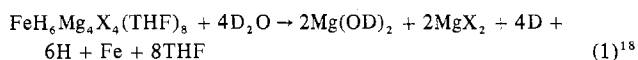[a] Standard deviation shown.

curred. The products from each of the above solubility experiments were analyzed for iron and magnesium and the results recorded in Table II on the rows labeled run 6 and run 7.

Treatment of YCS with pyridine immediately resulted in formation of metallic iron and hydrogen.

Discussion

YCS Composition. The mole ratio of iron, hydridic hydrogen, magnesium, halide, and THF is 1.00/6.00/4.03/4.13/7.86, respectively. The ratio was calculated from the average hydrolysis value for iron, hydridic hydrogen, magnesium, and halide and the highest pyrolysis value for THF. The YCS is formulated as $FeH_6Mg_4X_4(THF)_8$ where X_4 represents $Br_{3.39}Cl_{0.61}$. The compound is pure and its calculated molecular weight is 1029. The percentage of each component was calculated and shown with the average of the observed values in Table V.

The hydridic hydrogen content was calculated on the basis of the following reactions

$$FeH_6Mg_4X_4(THF)_8 + 4D_2O \rightarrow 2Mg(OD)_2 + 2MgX_2 + 4D + 6H + Fe + 8THF \qquad (1)^{18}$$

$$Fe + 2D_2O \rightarrow Fe(OD)_2 + D_2 \qquad (2)$$

Accordingly the H:D ratio would be 1.0. While this ratio was observed, the precision of the mass spectrometric determinations was insufficient to distinguish between the above reaction product and the possibility of further oxidation to iron(III). However, in the absence of air, such oxidation would not be expected. Furthermore, the reproducibility of the results and the physical appearance of both the wet and the desiccated product established that reaction 2 was quantitative.

The pyrolysis hydrogen values are useful to determine hydridic hydrogen content only if THF pyrolysis does not occur. The hydrogen values consisted of a group ranging from 0.647 to 0.668% and an outlying value of 0.810%. In pyrolysis 1, the very rapid heating of the YCS resulted in a low THF value and a high hydrogen value. The probable explanation was that THF pyrolysis occurred. It is known that THF polymerizes to low to moderate molecular weight glycols[19] and also dehydrates forming butadiene.[20] These reactions occur below 250 °C in the presence of a catalyst. Decomposition of the YCS yielded ultrafinely divided metallic iron, magnesium, and magnesium halide in the absence of air and water. These clean surfaces were probable catalysts for the polymerization and/or dehydration of THF to products of low volatility which remained in the hot reaction zone and ultimately pyrolyzed to hydrogen and carbon.
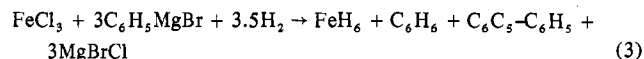
Comparison of pyrolysis 3 to 7 indicated THF pyrolysis in the former case. Specifically the percentage of the total hydrogen evolved was 1.10, 2.11, and 2.60% on heating pyrolysis 3 at 72 °C for 32 h, at 110 °C for 72 h, and at 135 °C for 17 h, respectively. In pyrolysis 7, the percentage of the total hydrogen evolved was 0.39, 1.05, and 2.17% on heating the sample for 72 h each at the temperatures 62, 105, and 135 °C, respectively. The smaller quantity of hydrogen produced despite the longer heating periods in pyrolysis 7 compared to 3 was evidence that THF decomposition occurred in pyrolysis 3. From this and the total hydrogen evolution,

it follows that THF decomposition occurred in pyrolyses 6 and 7 as well.

Pyrolyses 3 and 5 established that THF was tenaciously held in the reaction zone above 160 °C (Table IV). In pyrolysis 5, the heating period was about four times that of 3 and yet in both cases only 91% of the THF was evolved at 108 ± 2 °C and 96% at 155 ± 7 °C.
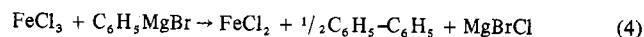
As it is probable that THF pyrolysis occurred to some extent in all the experiments, the high pyrolysis hydrogen values are rejected in favor of the more consistent values derived from the hydrolysis experiments and the maximum observed THF value is regarded as representing the minimum THF present.

Course of the Reaction. Weichselfelder[2] observed that about 3.5 mol of hydrogen was consumed per mole of iron present. He proposed the following equation

$$\text{FeCl}_3 + 3\text{C}_6\text{H}_5\text{MgBr} + 3.5\text{H}_2 \rightarrow \text{FeH}_6 + \text{C}_6\text{H}_6 + \text{C}_6\text{C}_5\text{-C}_6\text{H}_5 + 3\text{MgBrCl} \quad (3)$$
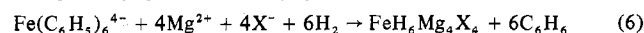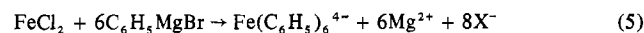
Since my primary objective in carrying out preparation 1 was to duplicate Weichselfelder's observations, reaction conditions were as nearly identical as possible. On the basis of eq 3, it was encouraging that hydrogen absorption corresponded to FeH$_{6.1}$. Hydrogen evolution upon hydrolysis of the entire reaction mixture corresponded to FeH$_{5.9}$. In the large-scale experiments, hydrogen absorption ranged from 3.5 to 4.2 mol/mol of iron.

The interpretation of the reaction is handicapped by insufficient data but several relationships are useful. The initial step did not involve direct reaction of iron(III) chloride with hydrogen and probably not the reaction of Grignard with hydrogen under these conditions.[21] The tenfold excess (for 1:1 reaction) of Grignard over iron(III) chloride indicated that the latter determined the extent of the hydrogen absorption. It is proposed that the initial step involved the reduction of iron(III) chloride by Grignard according to the equation

$$\text{FeCl}_3 + \text{C}_6\text{H}_5\text{MgBr} \rightarrow \text{FeCl}_2 + {}^1\!/_2\text{C}_6\text{H}_5\text{-C}_6\text{H}_5 + \text{MgBrCl} \quad (4)$$
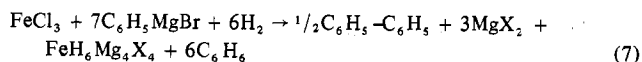
The formation of the tan precipitate (this work and ref 2, 5, and 7) and the ultimate hydridic product support the postulated initial reaction. The prolonged but finite hydrogen consumption indicated that the subsequently formed intermediates were relatively stable and reacted slowly. Equation 4 is apparently not consistent with the report that under a nitrogen atmosphere iron(II) chloride reacted relatively rapidly with phenyl Grignard to quantitatively form biphenyl and presumably metallic iron.[24]

The benzene formed in preparation 4 (Table I) was equal to the hydrogen consumed. Hydrogen is known to cleave the M-C$_6$H$_5$ bond to form the M-H bond and benzene. Typical compounds which exhibit this property are LiC$_6$H$_5$[22] and W(C$_6$H$_5$)$_4$(LiC$_6$H$_5$)$_2$·3(C$_2$H$_5$)$_2$O.[23] Thus, benzene formation is a measure of both the M-C bond cleavage and the M-H bond formation. The following reactions involving a complex iron-phenyl intermediate which is subsequently cleaved by hydrogen are tentatively proposed

$$\text{FeCl}_2 + 6\text{C}_6\text{H}_5\text{MgBr} \rightarrow \text{Fe(C}_6\text{H}_5)_6{}^{4-} + 6\text{Mg}^{2+} + 8\text{X}^- \quad (5)$$

$$\text{Fe(C}_6\text{H}_5)_6{}^{4-} + 4\text{Mg}^{2+} + 4\text{X}^- + 6\text{H}_2 \rightarrow \text{FeH}_6\text{Mg}_4\text{X}_4 + 6\text{C}_6\text{H}_6 \quad (6)$$

The overall reaction is thus

$$\text{FeCl}_3 + 7\text{C}_6\text{H}_5\text{MgBr} + 6\text{H}_2 \rightarrow {}^1\!/_2\text{C}_6\text{H}_5\text{-C}_6\text{H}_5 + 3\text{MgX}_2 + \text{FeH}_6\text{Mg}_4\text{X}_4 + 6\text{C}_6\text{H}_6 \quad (7)$$

In eq 5 through 7, X represents bromide plus chloride. The proposed Fe(C$_6$H$_5$)$_6{}^{4-}$ intermediate presumes that the hydride hydrogens in the YCS are bound to the iron atom. This is not necessarily the case.

From the reaction stoichiometry, i.e., the hydrogen consumed, the iron present, the benzene formed, and the Fe/H

Table VI. Hydrogen Absorption and Hydrolysis Results

Observer	H$_2$:Fe		Postulated compd
	H$_2$ absorbed	H$_2$ evolved	
Weichselfelder[2]	3.4–3.8	3.7–4.1	FeH$_6$
Takegami, Fujmaki[7]	3.5–4	3.4–4	Mg(FeH$_4$)$_2$
Gibbins	3.5–4.2	3.9^a	
Ray, Sahai[3]		2.5	FeH$_3$
Sarry[5]	5.3–11	2.1–3.1	FeH$_3$
Kost et al.[8]		3^b	

^{a} Preparation 1. ^{b} The black product.

mole ratio in the YCS, it is concluded that a large portion of the iron exists in some other form, probably metallic iron.

Comparison with Earlier Work. The ranges of hydrogen absorption and also of hydrogen evolution upon hydrolysis are shown in Table VI. The postulated hydridic compound (Table VI) was based upon the assumption that hydrolysis resulted in the quantitative formation of iron(II) hydroxide. In the upper three cases (Table VI), either the entire reaction mixture or an aliquot thereof was hydrolyzed. In the lower group of three, purification techniques were applied. The black appearance of the products was evidence that metallic iron was present in all cases. The smaller hydrolysis H$_2$:Fe mole ratio for the lower group compared to the upper group indicated that the purification techniques probably resulted in hydride decomposition rather than concentration of the iron. Kost et al.[8] stated that sample weights could not be obtained because the very reactive hydride decomposed in the drybox. They, as the others, reported only Fe:H mole ratios. Ray and Sahai[3] washed their product with diethyl ether. Sarry[5] washed her product with pyridine. The conditions described in all three cases would be expected to result in extensive hydride decomposition.

The results observed by Weichselfelder,[2] Takegami and Fujmaki,[7] and Gibbins (preparation 1, Table I) can be explained if it is assumed that iron existed only in the YCS and as the free metal and that hydrogen reacted to form only the YCS and benzene. If these assumptions are applied to preparation 4 of this report it is calculated that 62.3 mmol of YCS and 45.7 mmol of iron formed. If the entire mixture were hydrolyzed (eq 1 and 2), 420 mmol of hydrogen would be produced. The hydrolysis H$_2$:Fe mole ratio would be 3.9 which is near the average of the values reported for the hydrolysis of the crude reaction mixtures. If the assumptions were correct, then 30–50% of the YCS in preparation 4 was recovered.

The large hydrogen absorption values observed by Sarry[5] cannot be completely attributed to YCS formation even if it is assumed that all the iron is converted to the complex. On the basis of the H$_2$:Fe absorption and without isolating organic products, Sarry[5] suggested that the iron hydride catalytically hydrogenated the phenyl group. While this may have occurred in her experiments, the finite absorption of hydrogen, the excess of Grignard, and the isolation of benzene as the only volatile product indicated that hydrogenation was not a significant reaction in the work reported here. Evidence of the resistance of the phenyl group to hydrogenation under such reaction conditions was Takegami and Fujmaki's[7] observation that the product of styrene hydrogenation was ethylbenzene.

The pyrolysis properties of the hydridic products reported by previous workers varied widely. Sarry[5] concluded that hydride decomposition was complete below 300 °C and that organic contaminants pyrolyzed above 350 °C. I observed that with prolonged heating (715 h), 96% of the total hydrogen was evolved at 300 °C. Whether the remaining 4% was hydridic hydrogen or hydrogen from pyrolyzed THF was unknown. The problem of determining the hydrogen source might be solved by using deuterium in the hydride formation reaction.

Wiberg[5,6] reported that his FeH_6 was stable to 300 °C and was completely decomposed by 500 °C. Ray and Sahai[3] reported that the equilibrium dissociation pressure of the hydride FeH_3 was 3.5 cm at 20 °C and that at 60 °C it decomposed to FeH. This author cannot rationalize these last observations with his experience.

Nature of the YCS. There is no physical evidence for the structure or the bonding in the YCS. Attempts to obtain an infrared spectrum and thus establish the presence of an Fe–H bond failed due to decomposition. Kost et al.[8] reported an infrared spectrum for their white hydridic product and stated that there was no evidence for an Fe–H bond but rather an Mg–H bond. Such information serves only to indicate that there may be other hydridic products.

A possible structure is indicated by $Mg_4Br_6O[(C_2H_5)_2O]_4$[25] and similar compounds of beryllium.[26] It is suggested that the fundamental unit of the YCS molecule is a tetrahedron determined by the four magnesium atoms. A bridging hydrogen is on each edge and the iron atom is at the center of the tetrahedron. A halide atom is σ bonded to each magnesium atom. Two compounds consisting of four such tetrahedrally disposed metal atoms and bridging hydrogen atoms are $H_6Re_4(CO)_{12}{}^{2-}$[27] and $Co_4C_{20}H_{24}$.[28]

References and Notes

(1) A preliminary report was given at the Vth International Conference on Organometallic Chemistry, Moscow, Aug 1971, and at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971.
(2) T. Weichselfelder, *Justus Liebigs Ann. Chem.*, **447**, 64 (1926).
(3) R. C. Ray and R. B. N. Sahai, *J. Indian Chem. Soc.*, **23**, 67 (1946).
(4) C. Haenny and E. Levi, *Chimia*, **1/10**, 203 (1947).
(5) B. Sarry, *Z. Anorg. Allg. Chem.*, **288**, 48 (1956).
(6) J. Tullis, Office of Naval Research, London, European Scientific Notes, No. 7, 1953.
(7) Y. Takegami and T. Fujmaki, *Kogyo Kagaku Zasshi*, **64**, 741 (1961).
(8) M. E. Kost, N. N. Mal'tseva, and V. I. Mikheeva, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **9**, 576 (1964).
(9) A. P. Ginsberg, J. M. Miller, and E. Koubek, *J. Am. Chem. Soc.*, **83**, 4909 (1961).
(10) S. G. Gibbins, *J. Catal.*, **23**, 398 (1971).
(11) S. G. Gibbins, *Anal. Chim. Acta*, **56**, 486 (1971).
(12) S. G. Gibbins, *Anal. Chem.*, **43**, 1349 (1971).
(13) S. G. Gibbins, *Anal. Chem.*, **43**, 621 (1971).
(14) S. G. Gibbins, *Anal. Chim. Acta*, **60**, 242 (1972).
(15) S. G. Gibbins, *Anal. Chem.*, **43**, 295 (1971).
(16) S. G. Gibbins, *Anal. Chem.*, **43**, 1348 (1971).
(17) S. G. Gibbins, to be submitted for publication.
(18) Hydrogen and deuterium as H_2, HD, and D_2.
(19) H. Meerwein, *Angew. Chem.*, **59**, 168 (1947).
(20) I. G. Farbenindustrie A. -G., British Patent 506 038 (May 18, 1939); *Chem. Abstr.*, **33**, 93287 (1939).
(21) W. E. Becker and E. C. Ashby, *J. Org. Chem.*, **29**, 954 (1964).
(22) H. Gilman, A. L. Jacoby, and H. Ludeman, *J. Am. Chem. Soc.*, **60**, 2336 (1938).
(23) B. Sarry, M. Dettke, and H. Grossman, *Z. Anorg. Allg. Chem.*, **329**, 218 (1964).
(24) H. Gilman and M. Lichtenwalter, *J. Am. Chem. Soc.*, **61**, 957 (1939).
(25) G. Stucky and R. E. Rundle, *J. Am. Chem. Soc.*, **86**, 484 (1964).
(26) C. C. Addison and A. Walker, *J. Chem. Soc.*, 1220 (1963).
(27) H. D. Kaesz et al., *J. Am. Chem. Soc.*, **91**, 1021 (1969).
(28) J. Muller and H. Dorner, *Angew. Chem., Int. Ed. Engl.*, **12**, 843 (1973).

Effect of Steric Constraints on the Rates of Base Hydrolysis of Cobalt(III) Complexes

RICHARD A. HENDERSON and MARTIN L. TOBE*

The rate constants for the base hydrolysis of a number of cobalt(III) complexes of the type $[Co(L_4)Cl_2]^{n\pm}$ (L_4 is a linear quadridentate ligand containing two nonterminal secondary nitrogen donors) are reported. The α-cis isomers are some 10^4 times less reactive than the corresponding β-cis and trans species. The various factors contributing to the overall rate constants for base hydrolysis are considered, and it is concluded that the ability of the deprotonated (amido) nitrogen to become planar in the trigonal-bipyramidal intermediate and to orient its plane perpendicular to the trigonal plane of the cobalt is the major cause of this reactivity difference. The α-cis-$[Co(trien)Cl_2]^+$ cation (trien = 1,8-diamino-3,6-diazaoctane) is also some 10^4 times less reactive than its β-cis and trans isomers even though it possesses alternative sites for deprotonation. Compounds without nonterminal secondary amine donors do not exhibit this marked reduction of reactivity of the α-cis isomer. The effect of ring size is also discussed and the rules are applied to the reactivity pattern in a very extensive series of chloropentaminecobalt(III) complexes.

Introduction

The base-catalyzed hydrolysis of octahedral acidoaminecobalt(III) complexes has been shown to occur by a mechanism that involves the rapid dissociative solvolysis of the deprotonated amido conjugate base.[1,2] It has been suggested that the considerably enhanced lability of the conjugate base is due to strong π donation from the amido nitrogen to the cobalt in the trigonal-bipyramidal five-coordinate intermediate of the dissociative process[3] and it has been shown that, in the base hydrolysis of *trans*-$[Co(R,R(S,S)-2,3,2-tet)Cl_2]^+$ (2,3,2-tet = 1,9-diamino-3,7-diazanonane), the deprotonation is rate determining and takes place at one of the secondary nitrogens;[4] the initial reaction product, *trans*-$[Co(R,S-2,3,2-tet)OHCl]^+$,

is the same as that obtained from the R,S- (or meso) trans dichloro isomer.[5] In order to account for these results it was necessary to invoke a common intermediate. The β-cis-$[Co(R,R(S,S)-2,3,2-tet)Cl_2]^+$ isomer also yields the same product (presumably through the same intermediate) but, in this case, proton transfer is not rate determining.[6] The formation of a common intermediate from these three substrates requires that deprotonation takes place at a nitrogen that is the middle member of a meridional set of three donors and which we shall call "flat" for convenience and further requires that, in the five-coordinate intermediate formed by loss of chloride, (a) the cobalt is trigonal bipyramidal, (b) the amido group is planar, (c) the nitrogen lies in the trigonal plane