Contribution from the Istituto di Chimica Generale ed Inorganica, Università di Bari, Bari, Italy

Hidrido-complexes of Iron(IV) and Iron(II)

M. Aresta, P. Giannoccaro, M. Rossi, and A. Sacco

Received September 30, 1970

The preparation and properties are described of hydrido-complexes of iron(IV), FeH_4L_3 ($L = PEtPh_2$, $PBuPh_2$) and of iron(II), $FeH_2(PEtPh_2)_3$, $FeHCl(dp)_2$, $FeH_2(dp)_2$ [$dp = C_2H_4(PPh_2)_2$].

Introduction

Although some hydrido-complexes of osmium(IV) and ruthenium(IV) of general formula MH_4L_3 (L= tertiary phosphine) are known[1,2] analogous complexes of iron have not been described.

We have previously reported[3] that the reaction of iron(II) chloride dihydrate and tertiary phosphine with sodium borohydride in ethanol leads to the formation of hydrido-complexes of iron(II), FeH_2L_3. However, we now show that the yellow crystalline compounds obtained by the above reaction are tetrahydrido-complexes, FeH_4L_3, which in argon or helium slowly loose hydrogen to give the red dihydrido-complexes FeH_2L_3.

A number of hydrido-complexes of ruthenium(II) and osmium(II) of the type MHCl(diphosphine)$_2$ and MH$_2$(diphosphine)$_2$ (M = Ru, Os), are also known,[4] whereas only a very few analogous complexes of iron(II) have been described.[5] In contrast with what has been reported in literature,[5] we have found that the iron(II) chloride not only gives with the ligand $C_2H_4PPh_2)_2$, (dp), a well defined complex of formula $FeCl_2(dp)_2$, but also that the hydrido-complexes of formula $FeHCl(dp)_2$ and $FeH_2(dp)_2$ can be easily obtained in very good yields by reaction of the dichlorocomplex both with sodium borohydride in ethanol and with lithium aluminium hydride in tetrahydrofuran.

Experimental Section

All the solvents were of reagent grade quality and were dried, deaired and saturated with the suitable gas before use. All the reactions were carried out in an atmosphere of the specified pure gas by standard vacuum line techniques.

Sample for m.p. determination were contained in evacuated tubes. Infrared spectra were measured using a Perkin-Elmer 337 spectrometer. Gaschromatographic determinations were carried out using a Carlo Erba Fractovap Mod. B.N.m.r. spectra were determined on a Varian HA 100 using TMS as an internal reference.

Tetrahydridotris(n-butyldiphenylphosphine)iron(IV). $FeH_4(PBuPh_2)_3$. Iron(II) chloride dihydrate (0.65 g, 4.0 mmols) was dissolved in 30 ml of warm ethanol and added, under hydrogen atmosphere and stirring, to a solution of n-butyldiphenylphosphine (3.00 g, 12.35 mmols) in 10 ml of ethanol. To the slurry, obtained on cooling the reaction vessel to 0°C, was slowly added, in a countercurrent of hydrogen and under vigorous stirring, sodium borohydride (0.62 g, 16.4 mmols) partially dissolved in 10 ml of cold ethanol. After the addition was complete (about 1 hour), stirring was continued at 0°C until the initial red precipitate became yellow-brown (about 30 minutes). After filtration, the precipitate was washed twice with ethanol, dried in vacuo and extracted with 15 ml of benzene. The yellow solution was filtered and partially evaporated *in vacuo*; upon slow addition of ethanol the product was obtained in form of yellow crystals, which were washed with ethanol and dried in vacuo. (1.3 g, 41.4%) d.p. 88°C. *Anal.* Calcd. for $C_{48}H_{61}P_3Fe$: C, 73.4; H, 7.8; P, 11.8; Fe, 7.1. Found: C, 72.9; H, 8.0; P, 11.8; Fe, 7.1%.

Other preparations, carried out an atmosphere of argon, gave the same results.

Tetradeuteridotris(n-butyldiphenylphosphine)iron(IV). $FeD_4(PBuPh_2)_3$. This compound was similarly prepared from iron(II) chloride, n-butyldiphenylphosphine and sodium borodeuteride in deuteromethanol. The compound was also obtained from the corresponding hydrido-complex,both in the solid state and in benzene solution, by exchange with deuterium at room temperature and atmospheric pressure.

Tetrahydridotris (ethyldiphenylphosphine) iron (IV). $FeH_4(PEtPt_2)_3$. Iron(II) chloride dihydrate (0.82 g, 5.0 mmols) was dissolved in 20 ml of warm ethanol and added, under hydrogen atmosphere and stirring, to a solution of ethyldiphenylphosphine (3.30 g. 15.4 mmols) in 10 ml of ethanol. To the slurry, obtained on cooling the reaction vessel to −30°C, was slowly added, in a countercurrent of hydrogen and under vigorous stirring, sodium borohydride (0.80 g, 21.1 mmoles) partially dissolved in 10 ml of cold ethanol. After the addition was complete (about 1 hour), stirring was continued at −30°C until the initial red precipitate became yellow-orange (about 2 hours). After filtration at −30°C, the precipitate was washed twice with cold ethanol, dried in vacuo at room temperature

---

(1) P. G. Douglas and B. L Shaw, *J. Chem. Soc.* (A), 334 (1970).
(2) W. H. Knoth, *J. Am. Chem. Soc.*, *90*, 7172 (1968).
(3) A. Sacco and M. Aresta, *Chem. Comm.*, 1223 (1968).
(4) J Chatt and R. G. Hayter, *J. Chem. Soc.*, 2605 (1961).
(5) J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 5507 (1961).

and extracted with 15 ml of benzene. The orange solution was filtered and evaporated in vacuo, living a red oil. Ethanol (5 ml) was added, and the crystallization was induced by stirring and cooling to –30°C. When yellow crystals appeared, further ethanol (15 ml) was added, and the mixture allowed to stand at –30°C for some hours. The yellow crystals were filtered at room temperature, washed twice with ethanol, twice with light petroleum and recrystallized from benzene by adding light petroleum (1.35 g, 38.3%) d.p. 80°C.

Anal. Calcd. for $C_{42}H_{49}P_3Fe$: C, 71.9; H, 7.0; P, 13.2; Fe, 7.9. Found: C, 71.4; H, 6.8; P, 13.1; Fe, 7.8%.

Tetradeuteridotris(ethyldiphenylphosphine)iron(IV). $FeD_4(PEtPt_2)_2$. The compound was obtained from the corresponding hydrido-complex, both in the solid state and in benzene solution, by exchange with deuterium at room temperature and atmospheric pressure.

Dihydridotris(ethyldiphenylphosphine)iron(II). $FeH_2(PEtPh_2)_3$. Helium, saturated with n-pentane, was bubbled for about 12 hours through a suspension of tetrahydrido(ethyldiphenylphosphine)iron(IV) (1.0 g) in 10 ml of n-pentane at room temperature and in the dark. The yellow complex slowly dissolved to give a red solution, which was filtered and cooled at –80°C. On standing, red crystals were obtained in low yield.

Anal. Calcd. for $C_{42}H_{47}P_3Fe$: P, 13.3; Fe, 8.0. Found: P, 12.9; Fe, 7.4%

A concentrated solution of the product in n-pentane, treated with hydrogen at 0°C and atmospheric pressure, gave a yellow crystalline precipitate, identified as $FeH_4(PEtPh_2)_3$ by means of its I.R. spectrum. Another sample of the solution, treated with nitrogen at room temperature and atmospheric pressure, gave a yellow crystalline precipitate, identified as $FeH_2(N_2)(PEtPh_2)_3$ by means of its I.R. spectrum.[3,6]

Hydridochlorodi}1,2-bis(diphenylphosphino)ethane}-iron(II). $FeHCl(dp)_2$. To a mixture of diphosphine (1.70 g, 4.26 mmols) and iron(II) chloride dihydrate (0.346 g, 2.12 mmoles) in 25 ml of ethanol was slowly added at 50°C in a countercurrent of argon or nitrogen and under vigorous stirring, a solution of sodium borohydride (0.09-0.10 g, 1.1-1.2 mmols) in 20 ml of ethanol. The stirring was continued until the precipitate became red (about 90 minutes), then the product was filtered, washed with water and with ethanol at 40°C, dried in vacuo and recrystallized from benzene by adding ethanol. (1.7 g, 90%) d.p. 195°C.

Anal. Calcd. for $C_{52}H_{49}ClP_4Fe$: Cl, 4.0; P, 13.9; Fe, 6.30. Found: Cl, 4.1; P, 13.6; Fe, 6.25%.

Dihydridodi}1,2-bis(diphenylphosphino)ethane}iron-(II). $FeH_2(dp)_2$.

a) The compound was prepared in a similar manner, but using an excess of sodium borohydride (molar ratio $NaBH_4/Fe = 2.5\text{-}3$). The yellow precipitate was crystallized from benzene by adding pentane. D.p. 187°C.

Anal. Calcd. for $C_{52}H_{50}P_4Fe$: P, 14.5; Fe, 6.5. Found: P, 14.3; Fe, 6.4%.

b) To a solution of $FeCl_2(dp)_2$ (1.1 g, 1.2 mmols) in 30 ml of tetrahydrofuran was added at room temperature in a countercurrent of nitrogen and under stirring, lithium aluminium hydride (0,20 g, 2.4 mmols). An intensely red solution was first obtained, fading to pale yellow after stirring at room temperature for several hours. The solvent was removed in vacuo and the residue crystallised from benzene to give the pure product as yellow crystals (74%). Found: P, 14.4; Fe, 6.4%.

Dichlorodi}1,2-bis(diphenylphosphino)ethane}iron-(II). $FeCl_2(dp)_2$. A mixture of anhydrous iron(II) chloride (0.39 g, 3.1 mmols) and diphosphine (2.64 g, 6.6 mmols) in 60 ml of benzene was refluxed under a nitrogen atmosphere for several hours. The ferrous chloride dissolved to give a pale solution from which, by cooling or by adding pentane, the product precipitated as whitish crystals.

Anal. Calcd. for $C_{52}H_{48}Cl_2P_4Fe$: Cl, 7.7; P, 13.4; Fe, 6.0. Found: Cl, 7.5; P, 13.0; Fe, 6.0%.

Determination of the hydridic hydrogen. Samples of the hydrido-complexes were treated, in current of argon, with an excess of the reagent in an apparatus connected to the gaschromatographic apparatus, as previously described (7). Table I shows the results.

Results and Discussion

Tetrahydrido-complexes. They are pale yellow crystalline compounds, unstable to air, soluble in non polar solvents such as benzene, toluene, or tetrahydrofuran, insoluble in methanol, ethanol or petroleum ether.

Their I.R. spectra show sharp absorption bands assignable to Fe–H stretching (Table II): in Nujol mull, the complex with butyldiphenylphosphine shows four bands, whereas that with ethyldiphenylphosphine shows only two bands within the range 1850-1950 cm^{-1}; beside these bands surely assignable to Fe–H stretching, both complexes show a weak and large band at 2380-2400 cm^{-1}.

This band is not due to some borohydride impurity, like R_3PBH_3, because the analyses of the recrystallised complexes show the complete absence of the boron; moreover, this band disappears in the dihydrido-complex $FeH_2(PEtPh_2)_3$, obtained from the corresponding tetrahydrido-complex, and it reappears when the dihydrido-complex is converted in the tetrahydrido-complex by reaction with hydrogen.

Although at the moment we are not able to give an exact assignment to this band, it is surely bound to the presence of four hydridic hydrogen atoms in the complex.

In solution, both complexes show only one strong and large band at 1880 cm^{-1}. This behaviour shows an equivalence, most probably due to a rapid intramolecular process, of all the four hydrogen atoms, and this is confirmed by the n.m.r. spectrum of the complex with butyldiphenylphosphine, which shows at 22.1 τ a 1:3:3:1 quartet ($J_{P-H} = 27$ c.p.s.). A similar

---

(6) M. Aresta, P. Giannoccaro, M. Rossi, and A. Sacco, *Inorg. Chim. Acta*, this volume, in the press.

Table I. Analytic Results.

Compound	μ mols	Reagent	T (°C)	H_2 evolved, μ mols	Ratio H_2/Fe
$FeH_4(PEtPh_2)_3$	21.6	Heat	150	28.6	1.32
$FeH_4(PEtPh_2)_3$	32.5	Heat	150	52.0	1.60
$FeH_4(PEtPh_2)_3$	32.1	I_2 in C_6H_6	20	48.1	1.50
$FeH_4(PEtPh_2)_3$	41.3	Solid I_2	60	77.2	1.87
	31.2	N_2 (toluene)	20	31.5	1.01
$FeH_4(PEtPh_2)_3$	34.7	dp (toluene)	100	34.5	0.99
$FeH_4(PBuPh_2)_3$	33.3	Heat	120	46.4	1.39
$FeH_4(PBuPh_2)_3$	27.6	Heat	120	42.9	1.55
$FeH_4(PBuPh_2)_3$	39.8	Solid I_2	60	78.0	1.96
$FeH_4(PBuPh_2)_3$	29.3	Solid I_2	60	57.5	1.96
$FeH_4(PBuPh_2)_3$	22.5	HCl aq.	50	65.3	2.90
$FeH_4(PBuPh_2)_3$	29.0	HCl aq.	50	84.5	2.92
$FeHCl(dp)_2$	26.2	I_2 in C_6H_6	22	3.0	0.11
$FeHCl(dp)_2$	23.1	Solid I_2	60	11.4	0.49
$FeHCl(dp)_2$	22.6	Solid I_2	60	11.6	0.51
$FeH_2(dp)_2$	19.3	I_2 in C_6H_6	21	8.5	0.44
$FeH_2(dp)_2$	17.6	Solid I_2	60	16.2	0.92

Table II. *I*nfrared Absorption Bands (cm^{-1}).

Compound	Solvent	νFe-H	Fe-D
$FeH_4(PEtPh_2)_3$	Nujol mull	2380 w,l, 1922 m, 1860 s	
$FeH_4(PEtPh_2)_3$	C_6H_6	1880 s,l	
$FeD_4(PEtPh_2)_3$	Nujol mull		1380 m, 1340 s
$FeH_4(PBuPh_2)_3$	Nujol mull	2400 w,l, 1948 m, 1920 m, 1900 m, 1850 s	
$FeH_4(PBuPh_2)_3$	C_6H_6	1880 s,l	
$FeD_4(PBuPh_2)_3$	Nujol mull		1330 s
$FeH_2(PEtPh_2)_3$	oil	1950 m, 1890 m	
$FeHCl(dp)_2$	Nujol mull	1920 m	
$FeH_2(dp)_2$	Nujol mull	1870 s, 1845 s	
$FeH_2(dp)_2$	CH_2Cl_2	1875 m,l, 1825 m.l	

behaviour is shown by the corresponding osmium complexes.[1]

Tetradeuterido-complexes. On treating the tetrahydrido-complexes with deuterium, both in solution and in the solid state, a very slow exchange takes place (see Table II). In solution the exchange was completed after several days, and in the solid state after some months.

Hydrido-complexes of iron(II). The dihydrido-complexes of the type FeH_2L_3 are very soluble in all the organic solvents and they are usually obtained as red oils by bubbling an inert gas, like helium or argon, through the corresponding powdered tetrahydrido-complexes, according to the reversible reaction:

$$FeH_4L_3 \rightleftharpoons FeH_2L_3 + H_2 \qquad (1)$$

The dihydrido-complex of Formula $FeH_2(dp)_2$ is a very stable yellow crystalline compound, slightly soluble in benzene, soluble in tetrahydrofuran or methylene chloride,.insoluble in ethanol or petroleum ether. Its I.R. spectrum shows two bands ascribable to Fe–H stretching: at 1870 and 1845 cm^{-1} in Nujol mull, and at 1875 and 1825 cm^{-1} in methylene chloride solution. On the grounds of these values, we suggest an octahedral *cis*-configuration for the complex. In fact, all the known hydrido-complexes in which two hydride ligands are in the *trans*-configuration, namely those of the type $FeH_2(diphosphine)_2$,[5] $RuH_2(diphosphine)_2$,[4] $OsH_2(diphosphine)_2$,[4] $IrH_3(PR_3)_3$,[8] $CoH_3(PPh_3)_3$,[7] show a metal-hydrogen stretching in the range 1615-1770 cm^{-1}. By the contrast, the compounds of the type $RuH_2(PR_3)_4$[9] and $OsH_2(PR_3)_4$,[10] for which the n.m.r. data strongly suggest a *cis*-configuration, show a metal-hydrogen stretching in the range 1840-2000 cm^{-1}. The hydridochloro-complex of formula $FeHCl(dp)_2$ is a stable red crystalline compound, soluble in non-polar solvents such as benzene or tetrahydrofuran, insoluble in ethanol or petroleum ether.

Its I.R. spectrum shows a sharp absorption band at 1920 cm^{-1}, assignable to Fe–H stretching.

Reactions. The tetrahydrido-complexes react very easily with a number of reagents such as HCl, O_2, I_2, N_2, CO, CO_2, dp. On treating the complexes with solid iodine at 60°C, about 2 moles of hydrogen per mole of complex are evolved (see Table I), in agreement with the following equation:

$$FeH_4L_3 + I_2 = FeI_2L_2 + L + 2H_2 \qquad (2)$$

By reaction with iodine in benzene solution at room temperature a smaller amount of hydrogen is evolved, most probably owing to the formation of re-

---

(7) A. Sacco and M. Rossi, *Inorg. Chim. Acta*, *2*, 127 (1968).

(8) J Chatt, R. S. Cofter, and B. L. Shaw, *J. Chem. Soc.*, 7391 (1965).

(9) K. C. Dewhirst, W. Keim, and C. A. Reilly, *Inorg. Chem.*, *7*, 546 (1968).

(10) B. Bell, J. Chatt, and G. J. Leigh, *Chem. Comm.*, 576 (1970).

latively stable hydridoiodo-complexes:

$$FeH_4L_3+0.5I_2=FeHIL_3+1.5H_2 \qquad (3)$$

Such a behaviour is actually shown by $FeHCl(dp)_2$ and $FeH_2(dp)_2$, which in the same conditions give off only the 20-40% of the stoichiometric amount of hydrogen (see Table I).

On treating the tetrahydrido-complexes with an excess of concentrated hydrochloric acid, at temperatures higher than 50°C, about 3 moles of hydrogen are evolved per mole of complex (see Table I), in agreement with the following reaction:

$$FeH_4L_3+2HCl=FeCl_2+3L+3H_2 \qquad (4)$$

Also in this case a smaller amount of hydrogen is evolved when the reaction is carried out at lower temperatures.

On treating the tetrahydrido-complexes with nitrogen at room temperature one mole of hydrogen per mole of complex is evolved (see Table I), and the already described[3,6] dihydrido dinitrogen complex $FeH_2(N_2)L_3$, identified by means of its I.R. spectrum, is formed, according to the irreversible reaction:

$$FeH_4L_3+N_2\rightarrow FeH_2(N_2)L_3+H_2 \qquad (5)$$

On treating the tetrahydrido-complexes with an excess of the chelating diphosphine in toluene solution at about 100°C, one mole of hydrogen per mole of complex is evolved, and $FeH_2(dp)_2$, identified by means of its I.R. spectrum, is formed, according to the equation:

$$FeH_4L_3+2dp=FeH_2(dp)_2+3L+H_2 \qquad (6)$$

The amount of hydrogen evolved by thermal decomposition of the tetrahydrido-complexes is always less than 2 moles per mole of complex. A similar behaviour is shown by the trihydrido-complexes of cobalt[7] and it is very likely that it occurs for the same reason in both cases. However, no attempts were made to detect the presence of benzene or ethane (resp. butane) in the decomposition products.

Acknowledgments. This research was supported by the Consiglio Nazionale delle Ricerche.