

1079. *Some Hydrido-complexes of Iron(II).*

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Complexes of the type $[\text{FeCl}_2(\text{diphosphine})_2][\text{FeCl}_4]$ and $[\text{FeCl}_2(\text{diphosphine})_2]$ have been prepared from tertiary diphosphines of the types $\text{C}_2\text{H}_4(\text{PR}_2)_2$ ($\text{R} = \text{Me}$ or Et) and $o\text{-C}_6\text{H}_4(\text{PET}_2)_2$. From these were prepared monohydrides $[\text{FeHX}(\text{diphosphine})_2]$ ($\text{X} = \text{halogen}$) and a dihydride $[\text{FeH}_2\{o\text{-C}_6\text{H}_4(\text{PET}_2)_2\}_2]$ by reduction with lithium aluminium hydride. These have a band in the $1720\text{--}1880\text{ cm}^{-1}$ region due to $\nu_{\text{Fe-H}}$, and the Fe-hydrogen atoms show large chemical shifts (up to 39.1 p.p.m.; water standard) in the nuclear magnetic resonance spectrum. The hydrides are oxidised readily in air but show surprising thermal stability, which is attributed to the large ligand field strength of the phosphine ligands and hydride ion.

RECENT communications from these laboratories have reported the preparation of hydrides of the bivalent Group VIII metals Pt, Pd,¹ Fe², Ru,³ and Os,^{2,3} which are stabilised by co-ordination to tertiary phosphines and arsines. This paper describes some complexes of ditertiary phosphines with iron halides and their reduction to hydrido-complexes of iron(II). The only previously reported ligand-stabilised mononuclear iron hydrides are the well-known carbonyl hydride, $\text{FeH}_2(\text{CO})_4$, and $\text{FeH}(\text{CO})_2(\text{C}_5\text{H}_5)$.⁴

Only a very few complexes of iron(II) or iron(III) with tertiary phosphines or arsines are known,⁵ and the types most pertinent to this study are $[\text{FeCl}_2\{o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2\}_2][\text{FeCl}_4]$ and $[\text{FeX}_2\{o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2\}_2]$,⁶ whose phosphorus analogues we have obtained by reaction between anhydrous ferric or ferrous chloride and the ditertiary phosphines $\text{C}_2\text{H}_4(\text{PR}_2)_2$ ($\text{R} = \text{Me}$ or Et) and $o\text{-C}_6\text{H}_4(\text{PET}_2)_2$. The ligands $[\text{CH}_2]_n(\text{PPh}_2)_2$ ($n = 1$ or 2) also reacted, but the products were not well defined and readily dissociated. The ferric complexes $[\text{FeCl}_2(\text{diphosphine})_2][\text{FeCl}_4]$ are stable, dark red or green, crystalline, and soluble in polar organic solvents, in which they are ionised, but insoluble in water and hydrocarbons. They react vigorously with lithium aluminium hydride in tetrahydrofuran, with considerable decomposition and precipitation of black solids, probably containing metallic iron. Only the complex $[\text{FeCl}_2\{o\text{-C}_6\text{H}_4(\text{PET}_2)_2\}][\text{FeCl}_4]$ yields a crystalline product, $trans\text{-}[\text{FeH}_2\{o\text{-C}_6\text{H}_4(\text{PET}_2)_2\}_2]$, in 5% yield.

The ferrous complexes, $trans\text{-}[\text{FeCl}_2(\text{diphosphine})_2]$, are green, crystalline, and analogous to, although less stable and more reactive than, the corresponding complexes of ruthenium(II) and osmium(II).⁷ They are soluble in non-polar solvents and the $\text{C}_2\text{H}_4(\text{PR}_2)_2$

¹ Chatt, Duncanson, and Shaw, *Proc. Chem. Soc.*, 1957, 343; *Chem. and Ind.*, 1958, 859.

² Chatt, Hart, and Hayter, *Nature*, 1960, 187, 55.

³ (a) Chatt and Hayter, *Proc. Chem. Soc.*, 1959, 153; (b) *J.*, 1961, 2605.

⁴ Green, Street, and Wilkinson, *Z. Naturforsch.*, 1959, 14b, 738.

⁵ Nyholm, *J. Proc. Roy. Soc. New South Wales*, 1944, 78, 229; Hieber and Floss, *Z. anorg. Chem.*, 1957, 291, 314; Naldini, *Gazzetta*, 1960, 90, 391, 1231.

⁶ Nyholm, *J.*, 1950, 851.

⁷ Chatt and Hayter, *J.*, 1961, 896.

complex decomposes rapidly in water or alcohol and slowly in moist air. The *trans*-configuration was confirmed by the low dipole moment (1.3 D) of the complex with the diphosphine $C_2H_4(PET_2)_2$.

Preparation of Hydrido-complexes.—The dihydride *trans*- $[FeH_2\{o-C_6H_4(PET_2)_2\}_2]$, identical with that formed by the reaction of the diphosphine on finely divided iron under hydrogen,⁸ was prepared in 70% yield by reduction of *trans*- $[FeCl_2\{o-C_6H_4(PET_2)_2\}_2]$ with lithium aluminium hydride in tetrahydrofuran. Attempts to stop this reaction at the intermediate hydrido-chloride complex were not successful. However, similar reduction of *trans*- $[FeCl_2\{C_2H_4(PR_2)_2\}_2]$ (R = Me or Et) proceeds *via* the red hydridochloride and the reaction can be stopped at this stage by adding ethanol, evaporating the solution, and extracting the product from the solid residue. Further reduction of the hydrido-chlorides derived from the aliphatic diphosphines or isolation without the use of ethanol gave only yellow-orange oils. The infrared spectrum of the product from *trans*- $[FeHCl\{C_2H_4(PET_2)_2\}_2]$ showed a band at 1817 cm^{-1} , which may be due to the dihydride. *trans*- $[FeHI\{C_2H_4(PET_2)_2\}_2]$ was made by heating the corresponding hydrido-chloride with sodium iodide in acetone.

trans- $[FeHCl\{o-C_6H_4(PET_2)_2\}_2]$ was prepared by reaction between *trans*- $[FeH_2\{o-C_6H_4(PET_2)_2\}_2]$ and an equivalent of hydrogen chloride in ether. An unidentified white adduct (decomp. 80°) was first precipitated and this, on dissolution in acetone or ethanol, gave the desired hydrido-chloride in about 30% yield. The white product showed no band in its infrared spectrum attributable to ν_{Fe-H} . The properties of the hydrido-complexes are summarised in Table 1.

TABLE 1.

Compound	M. p.* (in vacuum)	Colour	Dipole moment (D)	ν_{Fe-H} (Nujol mull)	Chemical shift (p.p.m. H ₂ O standard), in C ₆ H ₆
<i>trans</i> - $[FeHCl\{C_2H_4(PMe_2)_2\}_2]$...	180°	Red	—	1810	—
<i>trans</i> - $[FeHCl\{C_2H_4(PET_2)_2\}_2]$...	154.5—155.5	Red	4.25	1849	+ 39.1
<i>trans</i> - $[FeHI\{C_2H_4(PET_2)_2\}_2]$...	173	Red-brown	—	1872	+ 33.9
<i>trans</i> - $[FeHCl\{o-C_6H_4(PET_2)_2\}_2]$	230.5—231.5	Red	—	1870	+ 36.0

* With decomposition.

The iron hydrides are sensitive to oxidation, especially in solution, and were purified by crystallisation in a nitrogen-filled glove box. They are less stable thermally than the corresponding hydrides of ruthenium(II) and osmium(II).

Structure.—The iron hydrido-chlorides show chemical shifts, which are large even for transition-metal hydrides. Each proton resonance of the unique hydrogen atoms consists of five, sharp, equally spaced bands with intensities in the approximate ratios 1 : 4 : 6 : 4 : 1, consistent with coupling between the proton and four equivalent phosphorus nuclei each of spin $\frac{1}{2}$. This pattern confirms the *trans*-structure indicated by dipole-moment measurements. Nuclear resonance and the dipole moments have previously demonstrated *trans*-structures for all the hydrido-tertiary phosphine complexes of platinum, ruthenium, and osmium.

The characteristic infrared frequency due to ν_{Fe-H} occurs in the range 1810—1872 cm^{-1} for the hydrido-chlorides and at 1726 cm^{-1} for the dihydride. The change in frequency with change in ligand and halide anion is in the sense: $C_2H_4(PMe_2)_2 < C_2H_4(PET_2)_2 < o-C_6H_4(PET_2)_2$, and $Cl < I$, as observed in the ruthenium and osmium series, where this sequence was discussed.^{3b} The chemical shifts increase in the reverse direction.

The deuterido-complexes *trans*- $[FeDCl\{C_2H_4(PET_2)_2\}_2]$ and *trans*- $[FeD_2\{o-C_6H_4(PET_2)_2\}_2]$ were prepared by reduction of the corresponding dichloro-complexes with lithium aluminium deuteride in tetrahydrofuran.

⁸ Chatt and Hart, unpublished work.

The infrared spectra (Nujol mulls) of the deuterides showed bands due to $\nu_{\text{Fe-D}}$ (strong) and $\delta_{\text{Fe-D}}$ (weak and broad) shifted by factors of $\sim 2^{-\frac{1}{2}}$ from the corresponding hydrogen vibrations. The results are summarised in Table 2.

TABLE 2.

	ν_{FeH}	δ_{FeH}	ν_{FeD}	δ_{FeD}
<i>trans</i> -[Fe(H,D)Cl{C ₂ H ₄ (PEt ₂) ₂ }] ₂	1849	656	1336	536
<i>trans</i> -[Fe(H,D) ₂ { <i>o</i> -C ₆ H ₄ (PEt ₂) ₂ }] ₂	1726	716	1259	525

These hydrides are different in character from the iron carbonyl hydrides where the hydrogen is acidic; *e.g.*, the compound [FeH₂{*o*-C₆H₄(PEt₂)₂}]₂ is unaffected by treatment with metallic lithium in tetrahydrofuran, sodium in liquid ammonia, or dilute aqueous sodium hydroxide.⁸ Thus, whereas the carbonyl hydride behaves as if it were polarised in the sense $\overset{\delta-}{\text{Fe}}(\text{CO})_4\overset{\delta+}{\text{H}}_2$ and the salts K₂Fe(CO)₄ were derived from iron(−2), the diphosphine complex behaves more as the first member of a homologous series of iron alkyls derived from iron(II). This behaviour is similar to that of the planar complex phosphino-hydrides, -alkyls, and -aryl of bivalent platinum, palladium, and nickel.⁹

Thermal Stabilities.—The thermal stabilities of some complex ruthenium, osmium, and iron hydrides were compared by heating them in pairs in evacuated tubes from room temperature (20°) to their decomposition temperature (*ca.* 300°) at about 4½° per minute (Table 3). Some slight yellowing of the molten compound was sometimes observed before general decomposition with blackening occurred.

TABLE 3.

Vacuum melting and decomposition temperatures of *trans*-[MXY{C₂H₄(PEt₂)₂}]₂.

M	X = Y = Cl		X = H, Y = Cl		X = Y = H	
	Melts	Decomp.	Melts	Decomp.	Melts	Decomp.
Fe	170°	170°	155°	155°	—	—
Ru	275	330	175	310	150°	280°
Os			171	315	150	295

It has been proposed that the critical factor in determining the stability of alkyl and aryl compounds of metals with filled or nearly filled non-bonding *d*-orbitals may be the ligand field splitting in the molecule.^{9,10} The same argument should apply to these complex hydrides. This would explain why the thermal stability increases as the Group is ascended. The fact that the hydrido-chlorides or dihydrides of ruthenium and osmium are so similar in stability suggests that another factor becomes critical after the necessary ligand field stabilisation has been reached, and that this has been reached in the ruthenium complexes. The only isolated dihydride of iron [FeH₂{*o*-C₆H₄(PEt₂)₂}] decomposes at 248–254° and is more stable thermally than the corresponding halohydride (Table 1). This may also be explained on the above basis since hydrogen in these complexes has a larger ligand splitting than has the halogen.¹¹ On the other hand, in the ruthenium and osmium complexes where ligand field splitting is not the critical factor, the dihydrides are less stable thermally than the halohydrides.

EXPERIMENTAL

Microanalyses are by the Microanalytical Department of these Laboratories. M. p.s were in vacuum unless otherwise stated. The hydrides were prepared and handled in a nitrogen-filled glove box. Light petroleum had boiling range 60–80° and molar conductivities were determined in nitrobenzene at 20°.

*Dichlorodi-{*o*-phenylenebisdiethylphosphine}iron(III) tetrachloroferrate(III)* was prepared by

⁹ Chatt and Shaw, *J.*, 1960, 1718, and references therein.

¹⁰ Chatt and Shaw, *J.*, 1959, 705.

¹¹ Chatt and Hayter, *J.*, 1961, 772.

adding the diphosphine (0.475 g., 1.86 mmole) in benzene (10 ml.) to ferric chloride (0.294 g., 1.86 mmole) in ethanol (10 ml.). The dark green precipitate was washed with benzene and crystallised from acetone as black rods (dark green when crushed), m. p. 150—165 (decomp.) (Kofler hot-stage) (66%) [Found: C, 40.2; H, 5.85%; *M* (ebullioscopically in acetone), 426 (0.42% solution), 475 (0.86%). $C_{28}H_{48}Cl_6Fe_2P_4$ requires C, 40.4; H, 5.8%; *M*, 833], molar conductivity 21.5 ohm^{-1} ($3.2 \times 10^{-3}M$); the nitrobenzene solution was green by transmission and red by reflection. In organic solvents dilute solutions appear to be green, and stronger solutions magenta.

Similarly prepared were:

Dichlorodi-{1,2-bisdiethylphosphinoethane}iron(III) tetrachloroferrate(III), from ethanol as dark red needles (85%), m. p. 148.5—149.5° [Found: C, 32.4; H, 6.6%; *M* (ebullioscopically in acetone), 415 (0.45% solution), 421 (0.94%), 437 (1.3%). $C_{20}H_{48}Cl_6Fe_2P_4$ requires C, 32.6; H, 6.6%; *M*, 737], molar conductivity 20.7 ohm^{-1} ($6.6 \times 10^{-3}M$).

Dichlorodi-{1,2-bisdimethylphosphinoethane}iron(III) tetrachloroferrate(III), from ethanol as purple-red needles (76%), m. p. 236—236.5° (Found: C, 22.6; H, 5.2. $C_{12}H_{32}Cl_6Fe_2P_4$ requires C, 23.1; H, 5.2%), molar conductivity 22.5 ohm^{-1} ($3.8 \times 10^{-3}M$).

trans-Dichlorodi-{*o*-phenylenebisdiethylphosphine}iron(II).—Ferrous chloride tetrahydrate (0.40 g., 2.03 mmole) was dehydrated by azeotropic distillation with benzene during 24 hr. After addition of the diphosphine (1.03 g., 4.1 mmole), ferrous chloride dissolved in a further hour to give a green solution. The solvent was removed at 12 mm. and the residue crystallised from benzene as lime-green rods (60%), m. p. 190—194° (decomp.) (Found: C, 52.7; H, 7.6. $C_{28}H_{48}Cl_2FeP_4$ requires C, 52.9; H, 7.6%).

The following compounds were similarly prepared:

trans-Dichlorodi-{1,2-bisdiethylphosphinoethane}iron(II), from light petroleum as bright green needles (72%), m. p. 168—171.5° (decomp.) (Found: C, 44.3; H, 9.1. $C_{20}H_{48}Cl_2FeP_4$ requires C, 44.55; H, 9.0%).

trans-Dichlorodi-{1,2-bisdimethylphosphinoethane}iron(II), from benzene-light petroleum (1:1) as emerald-green prisms (60%), m. p. 255—270° (decomp.), becoming yellow and losing diphosphine (Found: C, 33.7; H, 7.4. $C_{12}H_{32}Cl_2FeP_4$ requires C, 33.75; H, 7.55%).

trans-Dihydridodi-{*o*-phenylenebisdiethylphosphine}iron(II).—*trans-Dichlorodi*-{*o*-phenylenebisdiethylphosphine}iron(II) (0.50 g.) was suspended in dry tetrahydrofuran (15 ml.) and treated with a solution of lithium aluminium hydride in tetrahydrofuran. The green complex dissolved to give an orange-red solution. When an excess of the hydride was present, the solution was refluxed for 10 min. After cooling, the solvent was removed in a nitrogen stream; the residue, on crystallisation from light petroleum, afforded the pure product in 70% yield as prisms, m. p. 248—254° (decomp.) (Found: C, 59.8; H, 8.9. Calc. for $C_{28}H_{50}FeP_4$: C, 59.4; H, 8.9%). This compound may also be prepared in about 5% yield by similar reduction of $[FeCl_2\{o-C_6H_4(PET_2)_2\}_2][FeCl_4]$, and was identified by its infrared spectrum (Nujol mull) and analysis (Found: C, 59.3; H, 8.9%).

trans-Hydridochlorodi-{*o*-phenylenebisdiethylphosphine}iron(II).—*trans-Dihydridodi*-{*o*-phenylenebisdiethylphosphine}iron(II) (0.15 g.) in benzene (10 ml.) was treated with one equivalent of hydrogen chloride in ether (1.5 ml.) to give a white precipitate (0.16 g.). This product, on being heated in a vacuum, underwent irreversible colour changes to orange (80°), red (150°), black (200°), and melted at 214—218°. It was insoluble in benzene and in light petroleum, but dissolved in boiling acetone or ethanol to give a red solution of the desired product. After refluxing for a few minutes, the solvent was removed and the residue crystallised from light petroleum, yielding the pure complex (32%) as needles (Found: C, 55.45; H, 8.1. $C_{28}H_{49}ClFeP_4$ requires C, 56.0; H, 8.2%).

trans-Hydridochlorodi-{1,2-bisdiethylphosphinoethane}iron(II).—*trans-Dichlorodi*-{1,2-bisdiethylphosphinoethane}iron(II) (1.0 g.) in dry tetrahydrofuran (20 ml.) was reduced with lithium aluminium hydride in tetrahydrofuran. An intensely red solution was first obtained, fading to pale yellow when an excess of the reagent was present. Ethanol was then added until effervescence ceased, the red colour being restored. The solvent was removed in a nitrogen stream; the residue, on crystallisation from light petroleum, afforded the pure product as needles (83%) [Found: C, 47.1, 48.2; H, 9.6, 9.9; Cl, 6.6, 7.05%; *M* (ebullioscopically in benzene), 526 (0.57% solution), 518 (1.2%), 519 (2.05%). $C_{20}H_{49}ClFeP_4$ requires C, 47.6; H, 9.8; Cl, 7.0%; *M*, 505].

trans-Hydridochlorodi-{1,2-bisdimethylphosphinoethane}iron(II) was analogously prepared as

feathery needles from light petroleum (55% yield) (Found: C, 36.05, 35.9; H, 8.2, 8.3. $C_{12}H_{33}ClFeP_4$ requires C, 36.7; H, 8.5%).

trans-Hydridoiododi-(1,2-bisdiethylphosphinoethane)iron(II).—*trans*-[FeHCl{C₂H₄(PEt₂)₂]₂] (0.20 g.) in acetone (10 ml.) was treated with sodium iodide (0.20 g.) in acetone (5 ml.). The solution immediately darkened from red to deep brown and deposited a white precipitate. After being shaken and warmed for 10 min., the solution was filtered and evaporated and the residue crystallised from light petroleum to give the pure *product* as rods (65%) (Found: C, 40.4; H, 8.3; I, 21.5. $C_{20}H_{49}FeIP_4$ requires C, 40.3; H, 8.3; I, 21.3%).

Dipole moments.

	$10^3\omega$	$\Delta\epsilon/\omega$	τ^P	ϵ^P	o^P	μ
<i>trans</i> -[FeCl ₂ {C ₂ H ₄ (PEt ₂) ₂] ₂]	1.388	0.882				
	5.407	0.813	206	150 *	33	1.3
<i>trans</i> -[FeHCl{C ₂ H ₄ (PEt ₂) ₂] ₂]	9.241	4.505				
	11.65	4.468	539	145 *	372	4.25

* Calc. from group refractivities. $-\Delta\nu/\omega$ was taken as 0.4.

The dipole moments (see Table) were determined as described in ref. 9 and the nuclear magnetic resonance and infrared spectra as in ref. 3b.

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