

The work on this liquidus curve and on the structure of SiB_4 will be continued. A three-dimensional Fourier synthesis is being carried out at the moment and the exact parameters will be published later.

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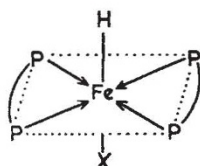
Some New Hydrides of Iron and Osmium

STABLE hydrido-complexes of the type $\text{trans-[MHX(phosphine)}_n\text{)]}$ ($X = \text{halogen or similar anionic ligand, phosphine} = \text{tertiary phosphine or chelate di-tertiary phosphine}$) containing the heavier transition metals ruthenium¹, osmium¹, palladium² and platinum² have been reported and a very unstable nickel derivative is also known³. Here we report the first stable derivatives containing a metal (iron) from the first transition series. These are interesting because the halo-hydrides (II) and (IV) show enormous chemical shifts in the proton resonance spectrum and because the hydride (I) was prepared from the metal and gaseous hydrogen. They have the *trans*-octahedral structure shown below and their properties are summarized in Table 1.

Table 1. PROPERTIES OF THE COMPLEX IRON HYDRIDES

Compound	m.p. (vacuum)	$\nu_{\text{Fe-H}}$ (Nujol mulls)	$\delta_{\text{Fe-H}}$ (Nujol mulls)	$\nu_{\text{Fe-D}}$ (Nujol mulls)	$\delta_{\text{Fe-D}}$ (Nujol mulls)	Chemical shift (p.p.m., water standard)
(I)	248-252° dec.	1,726(s)	716(m)	1,259(s)	525(m)	+18.4 (C_6H_6)
(II)	154.5-155.5° dec.	1,849(s)	—	1,336(s)	—	+39.1 (C_6H_6)
(III)	180° dec.	1,810(s)	—	—	—	+36.0 (C_6H_6)
(IV)	dec. c. 220°	1,870(s)	—	—	—	+36.0 (C_6H_6)

Trans- $[\text{FeH}_2\{o\text{-C}_6\text{H}_4(\text{PETe}_2)_2\}_2]$ (I) is prepared by dissolving finely divided iron in the diphosphine, $o\text{-C}_6\text{H}_4(\text{PETe}_2)_2$, at 190° under hydrogen at atmospheric pressure, or by reducing *trans*- $[\text{FeCl}_2\{o\text{-C}_6\text{H}_4(\text{PETe}_2)_2\}_2]$ or $[\text{FeCl}_2\{o\text{-C}_6\text{H}_4(\text{PETe}_2)_2\}_2][\text{FeCl}_4]$ with excess lithium aluminium hydride. It is an orange crystalline substance, easily soluble in organic solvents, monomeric in boiling benzene, and thermally remarkably stable but very sensitive to air. The red crystalline hydrido-chlorides (II) and (III) are obtained by lithium aluminium hydride reduction of *trans*- $[\text{FeCl}_2(\text{diphosphine})_2]$, while (IV) is made by the reaction of *trans*- $[\text{FeH}_2\{o\text{-C}_6\text{H}_4(\text{PETe}_2)_2\}_2]$ with one equivalent of hydrochloric acid in dry ether.



- (I) $X = \text{H}$, $\text{P-P} = o\text{-C}_6\text{H}_4(\text{PETe}_2)_2$
 (II) $X = \text{Cl}$, $\text{P-P} = o\text{-C}_6\text{H}_4(\text{PETe}_2)_2$
 (III) $X = \text{Cl}$, $\text{P-P} = o\text{-C}_6\text{H}_4(\text{PMe}_2)_2$
 (IV) $X = \text{Cl}$, $\text{P-P} = o\text{-C}_6\text{H}_4(\text{PETe}_2)_2$

Trans- $[\text{OsHCl}\{o\text{-C}_6\text{H}_4(\text{PETe}_2)_2\}_2]$, which completes the first eutropic series of phosphino-hydrides, has also been prepared, and a comparison of properties is made in Table 2.

Table 2. SOME PROPERTIES OF *trans*- $[\text{MHCl}\{o\text{-C}_6\text{H}_4(\text{PETe}_2)_2\}_2]$ ($M = \text{Fe, Ru, Os}$)

M	m.p. (vacuum)	Colour	Dipole moment (± 0.2 D)	$\nu_{\text{M-H}}$ (Nujol mull)	Chemical shift (p.p.m., water standard)
Fe	154.5-155.5 dec.	red	4.25	1,849	+39.1 (C_6H_6)
Ru	174.5-176	colourless	4.9	1,944	+27.1 (CHCl_3)
Os	170.5-171.5	colourless	4.6	2,051	+26.1 (C_6H_6) +31.3 (CHCl_3)

It will be noted that $\nu_{\text{M-H}}$ increases by 202 cm^{-1} on passing from $M = \text{iron}$ to $M = \text{osmium}$, corresponding to about 24 per cent increase in bond-strength (force constant) on ascending the series. This is also the sequence of increasing thermal stabilities.

The chemical shift of the proton resonance in compound (II) is the largest ever recorded. It is even greater than the shift of the proton resonance in water relative to the unshielded proton (27 p.p.m.).

We are indebted to Dr. N. Sheppard of the University of Cambridge for the nuclear magnetic resonance spectra, to Dr. D. M. Adams for the infra-red spectra and to Miss I. Bates for the dipole moment determinations.

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Gas Liquid Chromatography of Conjugated Fatty Acids

THE heating of polyunsaturated fatty acids in strong alkali is known to cause re-arrangement of the double bonds to form a conjugated system¹. The effect of this isomerization on the behaviour of polyunsaturated fatty acids in gas liquid chromatography has been studied in relation to linoleic and linolenic acids as found in wheat flour oil.

Oil was extracted by shaking the flour continuously for 2 hr. with carbon tetrachloride under nitrogen. The extract was filtered to remove flour particles and the solvent removed under vacuum in a rotary evaporator. Unconjugated fatty acids were prepared by saponification of the oil under nitrogen with 0.5 *N* methanolic potassium hydroxide, refluxing for 2 hr. Following acidification and ether extraction, the free fatty acids were methylated by reaction with diazomethane².

Conjugated fatty acids were prepared by an adaptation of the alkaline isomerization method³ for analysis of unsaturated fatty acids. The oil was heated in a solution of 6.6 per cent potassium hydroxide in ethylene glycol at 180° C. for 25 min. under a stream of oxygen-free nitrogen. The mixture was cooled, diluted with water and acidified, when the isomerized free fatty acids were extracted with ether. The fatty acids were methylated as before by reaction with diazomethane.

The mixed methyl esters were analysed with a Pye argon chromatograph using a column packed with 2.3 per cent poly(ethyleneglycol adipate) as stationary phase on 60-100 mesh diatomaceous earth (M. and B. 'Embacel'). The chromatograms of the