

with the exception of the cerium and promethium compounds. The good agreement between experimental and calculated lattice constant sustains the earlier observation of a linear relationship between end-member stannates.

TABLE I

Compound	Lattice constant Exptl.	Å. Calcd.	Calcd. density	Beige color of compound
Tb ₂ Sn ₂ O ₇	10.428 ± 0.005	10.430	7.815	Light
Dy ₂ Sn ₂ O ₇	10.389 ± .006	10.401	7.988	Dark
Ho ₂ Sn ₂ O ₇	10.374 ± .004	10.374	8.080	Light
Tm ₂ Sn ₂ O ₇	10.330 ± .003	10.326	8.281	Very light
Lu ₂ Sn ₂ O ₇	10.294 ± .004	10.286	8.515	Very light

U. S. ARMY SIGNAL RESEARCH AND DEVELOPMENT LABORATORY
FORT MONMOUTH, NEW JERSEY

CHARLES G. WHINFREY

ARTHUR TAUBER

RECEIVED DECEMBER 10, 1960

HYDRIDO COMPLEXES OF IRIDIUM

Sir:

While investigating routes to the lower oxidation states of some transition metals, we have obtained a series of compounds which appear to be hydrido complexes of iridium, $[\text{IrH}_n\text{X}_{3-n}\text{L}_3]$ ($n = 1, 2$; $\text{X} = \text{Cl}$ or Br ; $\text{L} = \text{Ph}_3\text{P}$, Ph_3As or Ph_3Sb). The compounds are prepared simply by heating an iridium salt and ligand with an alcohol (or aqueous alcohol), the mono-hydrido complexes readily being formed also at 25°. The latter are apparently related to those described recently^{1,2} since the commencement of the present studies. The new complexes are air-stable, diamagnetic and non-electrolytes, and some of their other properties are summarized in the table.

TABLE I

Compound	Color	M.p., °C. (dec. in vac.)	Infrared spectrum in 2000 cm. ⁻¹ region
$[\text{IrHCl}_2(\text{Ph}_3\text{P})_3]$	Yellow	256	2200 Deuteride 1580 ^a
$[\text{IrHCl}_2(\text{Ph}_3\text{As})_3]$	Yellow	240	2170
$[\text{IrHCl}_2(\text{Ph}_3\text{Sb})_3]$	Yellow- orange	201	2100
$[\text{IrH}_2\text{Cl}(\text{Ph}_3\text{P})_3]^b$	White	250	2215, 2110 Deuteride 1584, ^a 1515 ^a
$[\text{IrH}_2\text{Br}(\text{Ph}_3\text{P})_3]^b$	White	242	2240, 2090

^a $\nu_{\text{Ir-H}}/\nu_{\text{Ir-D}} = 1.39$ to 1.40 ; calcd., 1.41 . ^b Light sensitive.

Evidence for an Ir-H bond is obtained from infrared spectra: deuteration indicates that the sharp bands observed in the 2000 cm.⁻¹ region are associated with hydrogen vibrations, and their frequency suggests that they derive from $\nu_{\text{Ir-H}}$, by analogy with other hydrido complexes of transition metals.^{1,2,3}

$[\text{IrHCl}_2(\text{Ph}_3\text{P})_3]$ is best prepared (95% yield) from $(\text{NH}_4)_2\text{IrCl}_6$ and triphenylphosphine (6 moles) in aqueous 2-methoxyethanol at 100°. (Anal. Calcd. for $\text{IrCl}_2\text{P}_3\text{C}_{64}\text{H}_{46}$: Ir, 18.3; Cl, 6.7; P, 8.8; C, 61.7; H, 4.4. Found: Ir, 18.5; Cl, 6.5; P, 9.0; C, 61.2; H, 4.3.) The other mono-

(1) J. Chatt and B. L. Shaw, *Chem. and Ind.*, 931 (1960).

(2) J. Lewis, R. S. Nyholm and G. K. N. Reddy, *ibid.*, 1386 (1960).

(3) M. L. H. Green, *Angew. Chem.*, **72**, 719 (1960), and references quoted therein.

hydrido complexes given in the table were obtained under similar conditions or from aqueous ethanol or 2-ethoxyethanol. In these solvents at 25°, $[\text{IrHX}_2\text{L}_3]$ begins to precipitate after a few hours, a yield of 80% being obtained after several days or weeks. Halogen acid also has been detected in these reactions (hydride/acid $\cong 1/1$; cf. ref. 2).

Under more vigorous conditions, by heating $(\text{NH}_4)_2\text{IrCl}_6$ and triphenylphosphine (10–16 moles) in ethylene glycol to 190°, $[\text{IrH}_2\text{Cl}(\text{Ph}_3\text{P})_3]$ is formed in 87% yield. (Anal. Calcd. for $\text{IrClP}_3\text{C}_{64}\text{H}_{47}$: Ir, 18.9; Cl, 3.5; P, 9.1; C, 63.8; H, 4.7; mol. wt., 1017. Found: Ir, 18.6; Cl, 3.3; P, 9.0; C, 64.3; H, 4.8; mol. wt. in CHCl_3 , 997.) The corresponding bromide is obtained under identical conditions. (Anal. Calcd. for $\text{IrBrP}_3\text{C}_{64}\text{H}_{47}$: Ir, 18.1; Br, 7.5; P, 8.8; C, 61.1; H, 4.5; mol. wt., 1061. Found: Ir, 18.6; Br, 7.6; P, 8.7; C, 61.4; H, 4.4; mol. wt. in CHCl_3 , 1158.) These compounds represent the first dihydrido complexes of iridium, and probably of any metal synthesized under these simple conditions. The dideuterio complex was prepared by refluxing a suspension of $[\text{IrH}_2\text{Cl}(\text{Ph}_3\text{P})_3]$ in $\text{C}_2\text{H}_5\text{OD}$ for 10 days.

$[\text{IrH}_2\text{Cl}(\text{Ph}_3\text{P})_3]$ reacts slowly with HCl (in ether) to give $[\text{IrHCl}_2(\text{Ph}_3\text{P})_3]$, but the latter is remarkably resistant to acid at 30°. With excess chlorine (in CHCl_3), the dihydride is oxidized to $[\text{IrCl}_4(\text{Ph}_3\text{P})_2]$. Other isomers of each of the hydrides have been found and are being studied.

Experiments are continuing to investigate the role of the solvent in some of these unusual reactions and to examine the reactions and structures of the products. Dr. R. G. Hayter, to whom the author is indebted for valuable suggestions and discussions, has carried out further reductions of some of these compounds with LiAlH_4 and LiAlD_4 , and these will be reported later.

MELLON INSTITUTE
PITTSBURGH, PA.

L. VASKA

RECEIVED DECEMBER 12, 1960

17 α ,21-ISOPROPYLIDENEDIOXY STEROIDS

Sir:

This communication describes the preparation and use of a new protective group for the labile dihydroxyacetone side chain of the corticosteroids. It has been found that cyclic ketal formation occurs readily between the 17 α ,21-diol grouping of the cortical side chain and 2,2-dimethoxypropane in an acid catalyzed exchange reaction to give 17 α ,21-isopropylidenedioxypregnanes in good yields. A solution of 2 g. of prednisolone in 4 ml. of dimethylformamide and 15 ml. of 2,2-dimethoxypropane with 10 mg. of *p*-toluenesulfonic acid was heated for 6 hours to give 1.1 g. of 17 α ,21-isopropylidenedioxy-1,4-pregnadiene-3,20-dione-11 β -ol (I),¹ m.p. 243–247°, $[\alpha]_D +106^\circ$. Other corticoid derivatives prepared had these constants: 17 α ,21-iso-

(1) Satisfactory analyses have been obtained for all new compounds herein described. Ultraviolet absorption spectra are in 95% ethanol. Rotations are in chloroform and melting points are uncorrected. The isopropylidenedioxy derivatives display a characteristic infrared absorption band at 7.25 μ (chloroform).