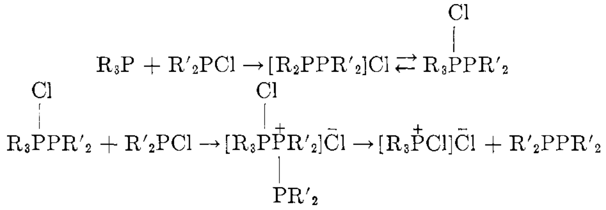
$CDCl_3$ solution of $[(C_2H_5)_3PP(C_6H_5)Cl]Cl$ at −20°. Peak C is assigned to phenyl protons; peaks E and F are attributable to the methylene and methyl protons, respectively, of the ethyl group. The broadness of peaks E and F is typical of the peaks observed in the ^1H nmr spectra of all adducts isolated in this study. The small peak, D, indicates a small concentration of triethyldichlorophosphorane at this temperature. The ^1H nmr spectrum observed for the above solution 15 min after it was allowed to warm to room temperature is represented by peaks G, H, I, and J in Figure 1(4). Changes of shape are noted for each of the peaks compared with the corresponding peaks above. The overlapping quartets and the two sets of triplets attributable to the methylene and methyl protons, respectively, of triethyldichlorophosphorane can be clearly seen in peaks H and J, respectively. These changes are more pronounced in the ^1H nmr spectrum obtained for the above solution after allowing it to stand at room temperature for 12 hr (Figure 1(5)). Peak M, corresponding to peaks E and I above, has nearly disappeared. Peak K, attributable to phenyl protons, may be compared with the ^1H nmr spectrum of tetraphenylcyclotetraphosphine, Figure 1(6), peak O, below. Peaks L and N may be compared with the ^1H nmr spectrum of an authentic sample of triethyldichlorophosphorane, peaks P and Q, Figure 1(7). Thus it appears that adduct formation is an intermediate step in the chlorine-abstraction process. A possible mechanism for the chlorine-abstraction reaction is represented by



$$R_3P + R'_2PCl \rightarrow [R_2PPR'_2]Cl \rightleftarrows R_3\overset{\displaystyle Cl}{\overset{|}{P}}PR'_2$$

$$R_3\overset{\displaystyle Cl}{\overset{|}{P}}PR'_2 + R'_2PCl \rightarrow [R_3\overset{\displaystyle Cl}{\overset{|}{P}}\underset{\underset{\displaystyle PR'_2}{|}}{\overset{+}{P}}R'_2]\overset{-}{Cl} \rightarrow [R_3\overset{+}{P}Cl]\overset{-}{Cl} + R'_2PPR'_2$$

where R = n-alkyl and R′ = C_6H_5.

The peaks observed in the ^{31}P nmr spectra of the new adducts are listed in Table II. The upfield signal is in the range from +14.7 to +51.0 ppm. The downfield signal is in the range from −14.5 to −33.7 ppm. The ^{31}P nmr spectrum of $[(C_4H_9)_3PAs(CH_3)_2]Cl$ exhibits a single peak at −16.2 ppm relative to 85% phosphoric acid.[20] The ^{31}P nmr shifts of a number of aminophosphonium salts are in the range from −29.4 to −54.0 ppm relative to 85% phosphoric acid.[21] These facts suggest that the downfield signals obtained for the adducts reported in this study are attributable to phosphonium phosphorus nuclei. If this is true, these adducts would be phosphinophosphonium chlorides and the upfield signals would be attributable to phosphino phosphorus nuclei.

TABLE II

Compound	^{31}P shifts relative to 85% phosphoric acid, ppm	Area ratio
$[(C_2H_5)_3PP(CH_3)_2]Cl$	+42.2, −33.7	1:1
$[(C_3H_7)_3PP(CH_3)_2]Cl$	+47.9, −22.5	1:1
$[(C_4H_9)_3PP(CH_3)_2]Cl$	+51.0, −21.2	1:1
$[(C_8H_{17})_3PP(CH_3)_2]Cl$	+25.9, −14.5	1:1
$[(C_4H_9)_3PP(CH_3)(Cl)]Cl$	+14.7, −16.5	1:1

The orange-red products isolated in the reactions of tri-n-alkylphosphines with phosphorus trichloride varied in their percentage of phosphorus from 88.79 to 92.42. The other elements present were carbon, hydrogen, and chlorine. These analytical results suggest that the orange-red materials were phosphorus networks having chlorine or organic end groups.

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The Preparation and Properties of Strontium Iridium Hydride[1]

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As part of a general study of ternary hydrides, we have examined the systems involving alkaline earth metals and the platinum metals. The systems Sr–Ir–H, Ca–Ir–H, Ca–Rh–H, Sr–Rh–H, Ca–Ru–H, and Sr–Ru–H all gave new ternary phases which appear to be related. This note describes the compound formed in the strontium–iridium–hydrogen system which has been studied most intensively. The compound is formed by heating a mixture of strontium hydride and iridium in a hydrogen atmosphere. No absorption of hydrogen was observed.

Ternary hydrides have been formed with alkali metals in combination with transition metals. The first to be reported were Li_4RhH_4 and Li_4RhH_5.[2] Graefe has described hydrides of lithium with rhodium, iridium, palladium, and platinum.[3] Magee and others have described lithium rhodium compounds in detail and have extended the lithium systems to include

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[1] R. O. Moyer, J. Tanaka, and R. Ward, Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, p 110-O.

[2] J. D. Farr, *J. Inorg. Nucl. Chem.*, **14**, 202 (1960).

[3] A. F. Graefe and R. K. Robeson, *J. Inorg. Nucl. Chem.*, **29**, 2917 (1967).

other transition elements.[4,5] Reilly and Wiswall have recently reported the system Mg–Ni–H.[6]

Experimental Section

Materials.—Strontium metal (98–99% from A. D. Mackay) was purified by vacuum distillation in a stainless steel apparatus. The distilled strontium was removed from the steel cold finger in a glove bag and broken into pieces with a cold chisel. The strontium chips were placed in a copper boat and heated to 600° for approximately 24 hr in a quartz tube filled with hydrogen at a pressure of 1 atm. The iridium powder (325 mesh and 99.9% from A. D. Mackay) was used as purchased.

Strontium Iridium Hydride.—The strontium hydride and iridium powder were thoroughly mixed in a mechanical shaker using agate balls and container. The powdered mixture was then pelleted at 5000 psi into a cylindrical pellet 0.25 in. in diameter and 0.125–0.25 in. in length. This pellet was then placed in a copper boat in a silica reaction tube and attached to a vacuum line. The system was then evacuated to better than 1×10^{-5} mm. Oxygen-free hydrogen was introduced into the system through a palladium tube. The hydrogen pressure varied from 658 to 631 mm depending on the run. The average pressure for 11 runs was 646 mm.

The reaction was carried out by heating the pellets to 800° for 8 hr. A strontium hydride to iridium mole ratio of 2:1 gave a single phase free from starting materials as shown by the X-ray powder patterns. All handling of the hydrides was carried out in a dry nitrogen atmosphere.

Chemical Analyses.—Strontium was determined gravimetrically as the sulfate. Hydrogen was determined by hydrolyzing the product in a vacuum line with dilute hydrochloric acid. The evolved hydrogen was transferred with a Toepler pump. The iridium, left as iridium metal after the decomposition with aqueous acid, was determined gravimetrically. *Anal.* Calcd for Sr_2IrH_4: Sr, 47.21; Ir, 51.75; H, 1.08. Found: Sr, 45.55; Ir, 52.7; H, 1.03. Calcd for SrH_2: H, 2.25. Found: H, 2.15.

Physical Properties.—Densities were measured by the liquid buoyancy method using carbon tetrachloride which was previously dried over calcium hydride.

X-Ray data were obtained with a GE XRD-5 diffractometer using Ni-filtered Cu radiation and a proportional counter. The sample was protected from the atmosphere by dispersing it in Vaseline on a glass microscope slide.

The magnetic susceptibility was measured by the Gouy method over a temperature range of 77–298°K and field strengths from 3.16×10^3 to 6.82×10^3 Oe.

Results and Discussion

Strontium iridium hydride is a black, crystalline, nonvolatile, nonsublimable solid. It reacts readily with water, evolving hydrogen.

The X-ray powder diffraction pattern was indexed on the basis of a cubic unit cell, $a = 7.62$ Å. The density was 5.46 g/cm³ as compared to the calculated value of 5.56 g/cm³ for four molecular formulas per unit cell.

A structure factor analysis of the X-ray data was made on the basis of strontium and iridium atoms only. Hydrogen atoms were excluded because of their relatively low X-ray scattering capacity. The results of the analysis shown in Table I appear to be consistent with the space group Fm3m. This suggests the fluorite structure with the following atomic coordinates: iridium at 0, 0, 0; 0, $^1/_2$, $^1/_2$; $^1/_2$, 0, $^1/_2$; $^1/_2$, $^1/_2$, 0; and strontium at $^1/_4$, $^1/_4$, $^1/_4$; $^3/_4$, $^1/_4$, $^1/_4$; $^1/_4$, $^3/_4$, $^1/_4$; $^3/_4$, $^3/_4$, $^3/_4$; $^1/_4$, $^1/_4$, $^3/_4$; $^3/_4$, $^1/_4$, $^3/_4$; $^3/_4$, $^3/_4$, $^1/_4$; $^1/_4$, $^3/_4$, $^3/_4$.

TABLE I

X-RAY DIFFRACTION POWDER DATA[a]

hkl	I_{obsd}	I_{calcd}	*hkl*	I_{obsd}	I_{calcd}
111	59.7	63.4	531	8.7	9.3
200	0.00	0.2	620	11.7	13.0
220	100	100	533	2.1	3.3
311	35.3	33.3	444	3.1	3.2
222	0.00	0.2	551, 711	4.4	5.1
400	17.8	17.0	642	12.7	10.3
331	12.8	13.9	553, 731	4.1	6.5
422	32.6	33.2	660, 822	10.4	10.3
511, 333	9.9	10.0	751, 555	4.4	5.0
440	10.9	9.7	840	7.3	5.1
			911, 753	6.1	7.2

[a] R(based on intensities) = 0.06.

A neutron diffraction analysis of strontium iridium deuteride is in progress. The result should clarify the structure of the ternary hydride phase.

Attempts were made to grow single crystals by heating the compound to 800° at pressures of 60–65 kbars in gold capsules. No crystals suitable for single-crystal X-ray study formed. Some transformation took place because the color changed from the black of the original product to a grayish white, and the X-ray powder pattern of the grayish white substance was no longer identical with the original product. Based on quantitative hydrolysis, no hydrogen was found in the grayish white product.

The magnetic susceptibility measurements of strontium iridium hydride indicated that it is weakly paramagnetic and is temperature independent from 77 to 298°K. The molar susceptibility after correcting for a small ferromagnetic impurity was 25×10^{-6}. The small ferromagnetic impurity was traced to the strontium hydride. It may have come from the steel system used to sublime the strontium metal. The magnetic susceptibility results are in accord with those reported by Lundberg, Cromer, and Magee,[5] who reported a weak temperature-independent paramagnetism ($\chi_m = 1.2 \times 10^{-6}$) in the temperature range 51–297°K for Li_4RhH_4. These results suggest metal–metal interaction.

A compressed pellet of strontium iridium hydride (0.25 in. in diameter and 0.25 in. in length) was placed between two probes of a Simpson voltmeter. The pellet was a poor electrical conductor at room temperatures. Values for electrical resistance greater than 2×10^{-7} ohm were obtained. Our crude conductivity measurements do not substantiate the metal–metal

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(4) F. C. Chang and C. B. Magee, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, p 144-M.

(5) L. B. Lundberg, D. T. Cromer, and C. B. Magee, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, p 145-M.

(6) J. L. Reilly and R. H. Wiswall, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, p 143-M.

interaction suggested by the susceptibility measurements. The failure to observe a higher conductivity may be due to surface contamination of the particles in the compacted powder. The contamination may arise from the inability to attain an absolutely inert atmosphere in the plastic glove bag which was used for handling the product.

An attempt was made to determine the infrared spectrum of the compound in a KBr pellet. No bands were observed in the 2000–2200-cm^{-1} range where the Ir–H stretch is reported to occur for the hydrido complexes of iridium,[7] but this may have been a limitation of the technique used.

The stoichiometery of the compound was initially indicated by the powder pattern data. When molar ratios of strontium hydride to iridium ranging from 2:1 to 5:3 are used, the resulting product gives rise to a characteristic X-ray powder pattern, and neither strontium hydride nor iridium can be detected in this powder pattern. Iridium was shown to be easily detected by X-ray analysis; free strontium hydride was not so easily observed. Experiments were carried out over a range of strontium hydride to iridium ratios of 10:1 to 1:2. These results indicate that the stoichiometry lies somewhere between an Sr: Ir mole ratio of 3:1 to 5:3. When either strontium hydride or iridium is used in amounts greater than indicated by the above ratio range, the characteristic lines for these constituents are seen in the X-ray powder pattern. Chemical analysis indicated material balance. There was no increase in the hydridic hydrogen. The analytical determinations showed that within experimental error the final product contained the same amount of hydridic hydrogen as the starting material. Uptake of hydrogen was also monitored. The early experiments showed a small decrease in hydrogen pressure, but this was also shown to occur in the system without reactants. Later experiments were carried out by not only regreasing the joint closest to the furnace before each run but also air cooling it during the run. This eliminated the loss of hydrogen and showed unequivocally that there was no hydrogen uptake during a reaction. The experimentally determined density and the size of the unit cell indicated that stoichiometry was two strontium hydrides to one iridium. These results are consistent with the stoichiometry of Li_4RhH_4 reported by Farr and Magee. However, unlike Magee, we have not been able to show the analog of the second hydride phase which he formulates as Li_4RhH_5.

A variety of conditions were tried for the synthetic procedure. The most favorable conditions seem to be a 24-hr heating period at 820°. At temperatures of 1000° the ternary phase undergoes decomposition. This was discovered when an attempt was made to prepare a pure compound by using an excess of strontium hydride, heating to destroy the strontium hydride preferentially, and distilling to remove the strontium. This procedure did not work since the ternary hydride was more easily decomposed than strontium hydride.

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Mass Spectral Studies of Metal Chelates. IV. Mass Spectra, Appearance Potentials, and Coordinate Bond Energies of Bis(acetylacetonate)metal(II) Complexes of the First Transition Series

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A number of papers dealing with the mass spectrometric investigation of metal β-diketonates have recently been published.[1–8] Here we report further results on the mass spectra of the bis acetylacetonates of Mn, Fe, Co, Ni, Cu, and Zn and the appearance potentials of selected ions derived therefrom.

Experimental Section

The acetylacetonates of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) were prepared by the aqueous solution synthesis of Fernelius and Bryant.[9]

The same procedure was used for Fe(acac)$_2$ except that zinc amalgam was also present to prevent oxidation of Fe(II) to Fe(III). Reagent grade acetylacetone was distilled before use. All samples, except Fe(acac)$_2$, were sublimed at least once before use. The mass spectral studies were performed on a Hitachi Perkin-Elmer RMU-6D single-focusing mass spectrometer using the techniques described previously.[6] For all of these samples the direct-insertion method was used, the sample being heated to 30–150° depending upon its volatility. The ionization chamber temperature was 150° for all reported experimental results, which, however, were insensitive to variations in chamber temperature.

Results

The mass spectra obtained for the chelates for 50-V electrons and an ionizing chamber temperature of 150°

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