Experimental Section

The ammoniate was prepared in a vacuum system by condensing known quantities of $Al(BH_4)_3$ and NH_3 in the reaction tube at liquid nitrogen temperature and allowing them to react at −80°. Excess NH_3 was distilled off. The product, a white powdery solid that is insoluble in hydrocarbons and ethers, had a composition consistent with the formula $Al(BH_4)_3 \cdot 6NH_3$. For nmr studies, 0.28 mmol of the ammoniate was prepared in a 5-mm o.d. tube and 5.22 mmol of liquid ammonia condensed over the sample. The composition of the resulting solution was about 5.4 mol % ammoniate. Boron-11 nmr spectra were obtained at 19.1 Mcps on a Varian DP-60 spectrometer using 2000-cps modulated side-band detection. Shifts were measured with $BF_3 \cdot O(C_2H_5)_2$ and $B(OCH_3)_3$ as external references. Hydrogen-1 nmr spectra were obtained on a Varian A-60 spectrometer over the range −60 to +40°. Shifts were essentially temperature independent. The signal to noise ratio improved at lower temperatures and it was found that the adduct was more soluble in NH_3 at lower temperatures. Peak areas were sensitive to radiofrequency power and side-band detection was used to minimize saturation and base-line drift.

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Complexes between Pyridine-2-carboxaldehyde 2′-Pyridylhydrazone and the Platinum Metals. II. Iridium

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We have recently described[1] complexes of 1,3-bis(2′-pyridyl)-1,2-diaza-2-propene (pyridine-2-carboxaldehyde 2′-pyridylhydrazone, PAPHY) and rhodium(III). In these complexes, the ligand is either tridentate or, when complexation is performed in aqueous solution of low pH, bidentate.

Several complexes of PAPHY and iridium(III) have now been synthesized using chloro complexes of iridium(III) or -(IV) as reactants, and the bidentate ligand function of PAPHY has been confirmed.

Experimental Section

Materials.—The ligand was purchased from the Aldrich Chemical Co., Inc., Milwaukee, Wis. Ammonium hexachloroiridate(IV) was supplied by International Nickel Co. Ltd., London. 1,2,6-Trichlorotris(pyridine)iridium(III) was prepared by Kauffmann's method.[2]

Apparatus.—Thermogravimetric analyses were performed on a Stanton TR-01 thermobalance (Stanton Instruments, London). Visible and ultraviolet absorption spectra were measured on an Optica recording spectrophotometer, CF4-N1, using matched 1-cm silica cells. Infrared spectra in the range 3500–500 cm^{-1} were recorded on a Grubb-Parsons double-beam grating spectrometer using the potassium bromide disk technique and in the range 500–200 cm^{-1} on a Hilger and Watts DM-4 spectrometer using Nujol mulls. Conductances were measured using a Doran conductivity bridge (Derritron Instruments Ltd., Stroud, England) with dip-type platinum-coated electrodes and approximately 10^{-3} *M* solutions in nitrobenzene, nitromethane, and water at 20°.

Analyses.—C, H, N, and Cl analyses were performed by F. Pascher and E. Pascher, Mikroanalytisches Laboratorium, Bonn, Germany. Iridium analyses were carried out by thermal decomposition of the complex to iridium metal under a hydrogen atmosphere.

Tris[1,3-bis(2′-pyridyl)-1,2-diaza-2-propene]iridium(III) Hexachloroiridate(III) Tetrahydrate (I).—A solution of 0.4370 g (1 mmol) of ammonium hexachloroiridate(IV) in 75 ml of water was refluxed for 2 hr with 0.3960 g (2 mmol) of PAPHY in 50 ml of chloroform. A red solid was deposited slowly and the chloroform layer became deep red. The precipitate was washed with water and ethanol and dried *in vacuo* over phosphorus pentoxide. Compound I was obtained as a deep red diamagnetic solid; yield 0.09 g. *Anal.* Calcd for $[Ir(C_{11}H_{10}N_4)_3][IrCl_6] \cdot 4H_2O$: C, 31.38; H, 3.01; N, 13.31; Cl, 16.85; Ir, 30.46. Found: C, 32.03; H, 2.53; N, 13.78; Cl, 17.10; Ir, 31.4. Thermogravimetric analysis showed a weight loss below 200° corresponding to four molecules of water. The molar conductance in nitromethane was 75.6 ohm^{-1} cm^2.

***cis*-Dichlorobis[1,3-bis(2′-pyridyl)-1,2-diaza-2-propene]iridium(III) Perchlorate Dihydrate (II).**—A mixture of 0.4370 g of ammonium hexachloroiridate(IV) and 0.3960 g of PAPHY was heated until it melted to a red liquid. This was maintained at 200° for 1 hr and then cooled; the solidified mass was extracted with four 50-ml portions of boiling water. The volume of the combined extracts was reduced to 50 ml by evaporation and a solution of 2 g of sodium perchlorate in 5 ml of water was added. The deep red solid which precipitated was filtered off, washed with small volumes of water and ethanol, and dried over phosphorus pentoxide; yield 0.15 g. *Anal.* Calcd for $[Ir(C_{11}H_{10}N_4)_2Cl_2]ClO_4 \cdot 2H_2O$: C, 33.2; H, 2.52; N, 14.1; Cl, 13.4. Found: C, 32.63; H, 2.67; N, 13.7; Cl, 13.7. Thermogravimetric and iridium analyses could not be carried out because of the explosive nature of II. The molar conductance in nitromethane was 98.5 ohm^{-1} cm^2.

***trans*-Dichloropyridine[1,3-bis(2′-pyridyl)-1,2-diaza-2-propenato]iridium(III) (III).**—A mixture of 1.01 g (2 mmol) of 1,2,6-trichlorotrispyridineiridium(III) and 0.3960 g (2 mmol) of PAPHY in 10 ml of ethanol was heated in a sealed tube at 200° for 80 hr during which time the initial yellow color of the solution changed to deep red. After cooling and filtering the contents of the tube, the filtrate was evaporated to yield a black solid. This was recrystallized several times from a 1:1 mixture of chloroform and ethanol and was isolated as a light brown diamagnetic solid; yield 0.35 g. *Anal.* Calcd for $Ir(C_{11}H_9N_4)(C_5H_5N)Cl_2$: C, 35.6; H, 2.60; N, 13.0; Cl, 13.1; Ir, 35.7. Found: C, 34.5; H, 2.60; N, 12.8; Cl, 13.9; Ir, 35.3. The molar conductance in nitromethane was 10.3 ohm^{-1} cm^2.

1,2,6-Trichloropyridine[1,3-bis(2′-pyridyl)-1,2-diaza-2-propene]iridium(III) Monohydrate (IV).—A mixture of 1.02 g (2 mmol) of ammonium *cis*-tetrachlorobis(pyridine)iridate(III)[2] and 0.396 g (2 mmol) of PAPHY in a 1:1 ethanol–water solution was refluxed for 8 hr. The reaction mixture was then further heated for 36 hr in a sealed tube at 150°. The deep red solution obtained was filtered and the filtrate was evaporated to 5 ml. A red diamagnetic solid crystallized out. This was recrystallized from 1:1 ethanol–water and dried over phosphorus pentoxide; yield 0.18 g. *Anal.* Calcd for $Ir(C_{11}H_{10}N_4)(C_5H_5N)Cl_3 \cdot H_2O$: C, 32.34; H, 2.86; N, 11.80; Cl, 17.95; Ir, 32.4. Found: C, 33.89; H, 2.95; N, 10.17; Cl, 17.7; Ir, 33.7. Thermogravimetric analysis showed a weight loss below 150° corresponding to one molecule of water. The molar conductance in nitromethane was 25.3 ohm^{-1} cm^2 for a 6.0×10^{-5} *M* solution.

Attempts to synthesize complexes of iridium from halogen-free

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[1] C. F. Bell and D. R. Rose, *Inorg. Chem.*, **7**, 325 (1968).

[2] G. B. Kauffmann, *Inorg. Syn.*, **7**, 228 (1963).

iridium compounds, for example, the hydrated oxides of iridium(III) and -(IV), were not successful.

Results and Discussion

Absorption Spectra.—Measurements were made on buffered aqueous solutions of II and III. Qualitative measurements only on IV were made owing to its very limited solubility and the insolubility of I precluded any measurements at all in solution.

Aqueous solutions of $[Ir(C_{11}H_{10}N_4)_2Cl_2]ClO_4 \cdot 2H_2O$ have a broad absorption band of λ_{max} 510 mμ at pH >5.1. Below this pH, a small hypsochromic shift is observed: λ_{max} 500 mμ at pH 2.3 and 490 mμ at pH 0.85. In the pH range 0.85–5.1, an isosbestic point is observed at 453 mμ. This is probably indicative of an equilibrium between $Ir(C_{11}H_{10}N_4)_2Cl_2^+$ and an ion such as $Ir(C_{11}H_{11}N_4)(C_{11}H_{10}N_4)Cl_2^{2+}$, in which the uncoordinated heterocyclic nitrogen atom of one of the PAPHY ligand molecules is protonated. ϵ_{max} is 2660 at pH 0.85 and 4120 at pH 8.9. The intensification of absorbance as the pH increases may be attributed to the loss of one or both of the imino-group protons to give $Ir(C_{11}H_{10}N_4)(C_{11}H_9N_4)Cl_2$ or $Ir(C_{11}H_9N_4)_2Cl_2^-$, respectively. Ion exchange confirmed the presence of a colored anion in alkaline solutions of II.

The spectra of $Ir(C_{11}H_9N_4)(C_5H_5N)Cl_2$ in aqueous solutions show continuously increasing absorption as the wavelength decreases below 450 mμ. The only feature worthy of note is a small shoulder at 300 mμ. Increased absorption occurs in the visible region as the pH is increased. The protonated complex $Ir(C_{11}H_{10}N_4)(C_5H_5N)Cl_2^+$ should be the main species at low pH; $Ir(C_{11}H_9N_4)(C_5H_5N)Cl_2$ will be the main species at high pH.

$Ir(C_{11}H_{10}N_4)(C_5H_5N)Cl_3$ in aqueous solution shows an absorption maximum at 510 mμ with a shoulder at 412.5 mμ. On addition of alkali, the band at 510 mμ becomes less intense and the shoulder becomes more intense.

Infrared Spectra.—Major bands in the spectra of the four iridium complexes are summarized in Table I. Assignments have been made on the basis of previous work with rhodium[1] and standard texts.[3,4]

Frequencies due to vibration of the ligand are typical of coordinated PAPHY. Thus pyridine I is increased by ⩾20 cm^{-1}, pyridine II is virtually unchanged, the C═N stretching frequency is lowered, and the "breathing" mode of the pyridine ring moves to a higher frequency compared with the positions of these bands in PAPHY itself.

The assignment of bands in the range 500–200 cm^{-1} is very helpful in formulating and deducing the stereochemistry of the complexes. Thus I contains $IrCl_6^{3-}$ ions because only one band is observed between 200 and 400 cm^{-1}. For this ion, two normal modes of vibration are infrared active (designated ν_3 and ν_4 by Adams[4]). ν_3 has been reported in the range 316–342 cm^{-1} and has been found to be strongly dependent on the cation present; ν_4 has been observed only below 200 cm^{-1}. The band at 305 cm^{-1} is therefore assigned to ν(Ir–Cl) in $IrCl_6^{3-}$. Alternative formulations of I would be *trans*-$[Ir(C_{11}H_{10}N_4)_2Cl_2][Ir(C_{11}H_{10}N_4)Cl_4] \cdot 4H_2O$ (Ia) or *cis*-$[Ir(C_{11}H_{10}N_4)_2Cl_2][Ir(C_{11}H_{10}N_4)Cl_4] \cdot 4H_2O$ (Ib). Ia would show one ν(Ir–Cl) due to the cation and four ν(Ir–Cl) due to the anion. Ib would show two ν(Ir–Cl) due to the cation and again four ν(Ir–Cl) due to the anion. Formulations Ia and Ib can, therefore, be eliminated as possible alternatives.

TABLE I

INFRARED DATA FOR COMPLEXES OF PAPHY AND IRIDIUM(III) (FREQUENCIES IN CM^{-1})

I	II	III	IV	Assignment
1607 s	1623 s	1613 s	1613 s	Pyridine I
1575 sh	1569 w	1577 w	1582 sh	Pyridine II
1538 w	1515 m	1527 w	1515 w	C═N?
1476 s	1498 m	1493 s	1471 s	Pyridine III
	1471 m			
1449 sh	1449 s	1453 s	1449 s	Pyridine IV
1434 s	1429 s		1437 s	
1023 m, 1000 b	1020 b	1020 w	1020 w	Breathing mode
			332 sh	
305 s	312 s	322 s	318 s	Ir—Cl
	293 sh		303 sh	
			270 m	Ir—N
		260 m	260 m	

The two ν(Ir–Cl) bands found for II are consistent with its formulation as the *cis* isomer.[5] In $Ir(C_{11}H_9N_4)(C_5H_5N)Cl_2$, the band at 260 cm^{-1} shows the presence of a coordinated pyridine molecule.[4] Another band, at 322 cm^{-1}, is attributed to ν(Ir–Cl). In view of the fact that octahedral *cis*-dichloro complexes typically show two bands due to ν(M–Cl) and the *trans* isomer shows one only, it appears that III is probably the *trans* isomer.

In $Ir(C_{11}H_{10}N_4)(C_5H_5N)Cl_3 \cdot H_2O$ there are three bands which may be attributed to ν(Ir–Cl) and two which may be attributed to ν(Ir–N), where N refers to coordinated pyridine. Three bands for ν(Ir–Cl) are expected for the 1,2,6 isomer and two for the 1,2,3 isomer. The second isomer has not been prepared so a comparative study of the spectra has not been possible and our conclusion that this is the 1,2,6 isomer must be regarded as tentative.

Conductances.—The conductance of II is within the range expected for 1:1 electrolyte[6] and confirms its formulation. III and IV are formulated as nonelectrolytes but their conductances indicate that dissociation into ionic species has occurred in nitromethane. It is possible that, as suggested for other systems,[7] displacement of chloride ion by nitromethane takes place to a limited extent

$$Ir(C_{11}H_9N_4)(C_5H_5N)Cl_2 + CH_3NO_2 = Ir(C_{11}H_9N_4)(C_5H_5N)Cl(CH_3NO_2)^+ + Cl^-$$

Conclusions

All four complexes contain iridium(III), as shown by their diamagnetism. When Ir(IV) is used as starting

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[4] D. M. Adams, "Metal-Ligand and Related Vibrations," E. Arnold, Ltd., London, 1967.

[5] R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, **4**, 350 (1965).

[6] N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

[7] R. A. Walton, *ibid.*, *A*, 1485 (1967).

material, reduction to Ir(III) by the ligand must accompany complexation.

PAPHY appears to be bidentate in I, II, and IV. $Ir(C_{11}H_{10}N_4)_3^{3+}$, the cation in I, is the analog of the Rh(III) complex ion described earlier.[1] The isolation of the *cis*-dichloro complex, II, is an illustration of the kinetic inertness to substitution shown by cationic complexes of iridium. Four of the chlorines in $IrCl_6^{3-}$ are replaced by two bidentate PAPHY molecules to produce the *cis*-dichlorobis(pyridine-2-carboxaldehyde 2′-pyridylhydrazone)iridium(III) cation, but further substitution of chlorines appears to be difficult. It has been reported that 1,10-phenanthroline reacts with $IrCl_6^{3-}$ to give similarly the *cis*-dichlorobis(1,10-phenanthroline)iridium(III) cation.[8]

The coordination behavior of PAPHY toward the three members of the cobalt subgroup in an oxidation state of +3 has now been established. Toward Co(III), it is tridentate.[9] Toward Rh(III), it can be either tri- or bidentate, although the tris complex containing bidentate PAPHY is labile in aqueous solution and readily changes to the bis complex. In three of the Ir(III) complexes reported here PAPHY appears to be bidentate, but tridentate in complex III.

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The Red and White Forms of Thorium Oxydiiodide and Their Transport Reactions[1]

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During an earlier study[2] of the synthesis and properties of the metallic thorium diiodide, traces of a remarkably voluminous, red product were found in the cooler ends of the tantalum container, well separated from the diiodide and thorium metal. Analytically, the material corresponded to the composition $ThOI_2$, and the amounts obtained were typically such as would result from an average oxygen contamination of only 100 ppm in the reactants. Since that time Scaife and coworkers[3] have described some of the properties of $ThOI_2$ as prepared by the direct reaction of thorium oxide and excess tetraiodide in a silica container at 600° followed by removal of the unreacted tetrahalide under vacuum. Their results contrasted with our earlier observations in two respects: their product was white rather than red, and they made no mention of the apparent sublimation or transport of the compound to cooler zones. The present paper describes work done to clarify the synthesis and interconversion reactions of the white and red forms and the character of the transport reaction.

Results and Discussion

Synthesis Reactions.—As before,[3] the *white*, acicular $ThOI_2$ is easily obtained by the direct reaction of unsintered ThO_2 and excess ThI_4 (or the elements), at 780–850° for several days followed by vacuum sublimation of the excess halide at 530°. In Vycor containers small amounts of SiI_4 and ThO_2 (on the walls) are sometimes produced by extensive heating at or above 850°, and the attack becomes substantial by 1000°. Tantalum is a generally more satisfactory container.

The *red* modification is always (and, to date, only) obtained after heating ThO_2 and ThI_4 reactants or white $ThOI_2$ in the presence of, but not necessarily in contact with, excess thorium metal (or ThI_2). This reaction is best accomplished in tantalum though on rare occasions the red form has been obtained in a Vycor apparatus. Oxide on the thorium (or tantalum) can also function as the sole oxygen source although at these temperatures the oxygen solubility and diffusion rate in thorium are too low to allow purification of more than the surface.

With either the red or the white form the product is usually found as a compact mat in which crystal growth is evident and as a crystalline mass of very low density which has obviously sublimed or been transported to the cooler end of the container. This transport also allows the colorless form to be separated after more complex reactions wherein silica furnishes the oxygen, such as from SiO_2 plus ThI_4 in tantalum at 850° or from ThI_4 plus thorium or tantalum in Vycor at 860° for several days. The second type of reaction with tantalum present gives the clearest indication of the course of the reaction. At least as long as ThI_4 is in excess, the $ThOI_2$ together with Ta_2Si are found on the tantalum while the volatile TaI_5 occurs throughout. The silica is transported to the metal, probably as SiI_4 and $TaOI_3$ judging from the simpler $Ta–I_2–SiO_2$ system.[4] The net reaction in the present system

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[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

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