into a solid cake. Raising the temperature to 200° resulted in no further change.

The black solid was moderately hygroscopic; it reacted with water and formed, first, an orange solid, and, finally, a green solution. Gas effervescence was noted during this reaction.

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Boron-11 Nuclear Magnetic Resonance Evidence for the Structure of $Al(BH_4)_3 \cdot 6NH_3$

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A number of interesting adducts of aluminum borohydride have been reported since the synthesis of this compound in 1940.[1] Extensive studies have been made of the reaction of $Al(BH_4)_3$ with trimethylamine which forms a 1:1 adduct[1-6] and which results in a cleavage of the $Al(BH_4)_3$ structure to form $(CH_3)_3NBH_3$ and various AlH_3 adducts when an excess of trimethylamine is added.[1-3,7] The reaction of $Al(BH_4)_3$ with ammonia to give a 1:1 adduct has been reported[1] as have reactions giving adducts of other stoichiometry.[1,7-11] We wish to report on our investigation of $Al(BH_4)_3 \cdot 6NH_3$, the structure of which appears to be quite different from those of the alkylamine adducts.

Results and Discussion

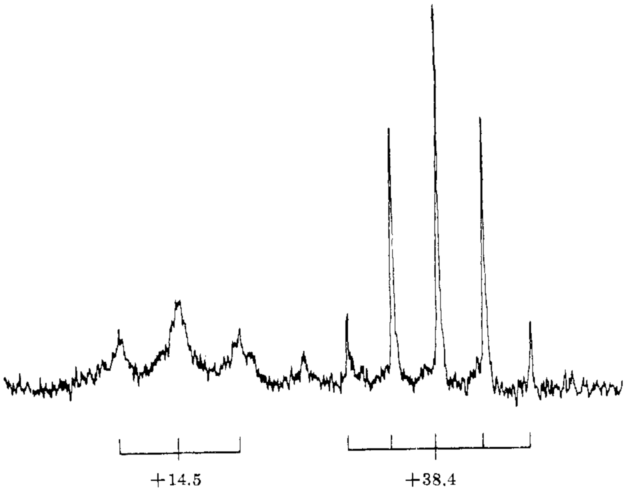

Figure 1.—Boron-11 magnetic resonance spectrum of $Al(BH_4)_3 \cdot 6NH_3$ at 19.1 MHz. Increasing magnetic field is to the right. Shifts are in ppm relative to $BF_3 \cdot O(C_2H_5)_2$.

The ^{11}B nmr spectrum of $Al(BH_4)_3 \cdot 6NH_3$ dissolved in liquid ammonia is shown in Figure 1. This spectrum bears a striking resemblance to that reported for the diammoniate of diborane.[12] The high-field quintet, with a chemical shift of +38.4 ppm relative to $BF_3 \cdot O(C_2H_5)_2$ and J_{BH} = 80 cps, is unmistakably the spectrum of the BH_4^- ion. The low-field triplet, evidence for $BH_2(NH_3)_2^+$, has a chemical shift of +14.5 ppm (in the diammoniate of diborane this was reported as +14.6 ppm[12]) and J_{BH} = 110 cps. No $^{27}Al-^{11}B$ coupling is observed in any part of the ^{11}B spectrum.[6] As in the case of the diborane ammoniate, the BH_4^- quintet is easily saturated. Using sufficiently low radiofrequency power to avoid saturation, rapid-passage electronic integration of the peak areas gave the ratio of BH_4^- to $BH_2(NH_3)_2^+$ borons as 2:1. This would suggest that the structure of $Al(BH_4)_3 \cdot 6NH_3$ might be $AlH_2(NH_3)_4{}^+BH_2(NH_3)_2{}^+(BH_4{}^-)_2$ where hexacoordinated Al^{3+} has been assumed. Chemical evidence, *via* the reaction of BH_4^- with NH_4Cl,[13] also supports the presence of two BH_4^- ions per single $Al(BH_4)_3 \cdot 6NH_3$ stoichiometric unit. The ^1H nmr spectrum shows a typical BH_4^- quartet, J_{BH} = 82 cps, with no evidence of the $^{27}Al-^1H$ coupling found in the 1:1 $(CH_3)_3N$ adduct.[6] A peak arising from bound NH_3 molecules is found 3.7 ppm below the solvent ammonia peak. The line width of this peak and that of the solvent are temperature dependent because of solvent–solute exchange. A small pair of peaks appears between the triplet and quintet in the ^{11}B spectrum. The area of these peaks is only about 0.02 that of the BH_4^- quintet. Their position and separation (95 cps) suggest they may be part of a quartet arising from the presence of a small amount of H_3NBH_3. The ^{11}B shifts reported for simple alkylamines lie in the range +9.1–+13.3 (in benzene and neat) and J_{BH} = 91–101 cps. The ionic structure of $Al(BH_4)_3 \cdot 6NH_3$, so far unreported for any other aluminum borohydride adduct, is consistent with the similar contrast between the reaction of tertiary amines and other electron donors with boron hydrides and the corresponding reactions of ammonia. In the former case, symmetric cleavage results in the formation of amine–boranes, while ammonia results in asymmetric cleavage to form ions.[14]

Further study of the structure of this ammoniate as well as several other related ammoniates is in progress and will be reported shortly.

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[1] H. I. Schlesinger, R. T. Sanderson, and A. B. Burg, *J. Am. Chem. Soc.*, **62**, 3421 (1940).

[2] J. K. Ruff, *Inorg. Chem.*, **2**, 515 (1963).

[3] P. H. Bird and M. G. H. Wallbridge, *J. Chem. Soc.*, 3923 (1965).

[4] N. A. Bailey, P. H. Bird, and M. G. H. Wallbridge, *Chem. Commun.*, 438 (1965).

[5] N. A. Bailey, P. H. Bird, and M. G. H. Wallbridge, *ibid.*, 286 (1966).

[6] P. C. Lauterbur, R. C. Hopkins, R. W. King, O. V. Ziebarth, and C. W. Heitsch, *Inorg. Chem.*, **7**, 1025 (1968).

[7] J. K. Ruff and M. F. Hawthorne, *J. Am. Chem. Soc.*, **82**, 2141 (1960).

[8] H. I. Schlesinger, H. C. Brown, and E. K. Hyde, *ibid.*, **75**, 209 (1953).

[9] A. E. Finholt, C. Helling, V. Imhof, L. Nielson, and E. Jacobson, *Inorg. Chem.*, **2**, 504 (1963).

[10] P. C. Maybury and L. Taylor, File No. Chem. 40-33, ASTIA Document Service Center, Arlington, Va., April 20, 1961, p 30.

[11] J. C. Fauroux and S. J. Teichner, *Bull. Soc. Chim. France*, 4053 (1967).

[12] T. P. Onak and I. Shapiro, *J. Chem. Phys.*, **32**, 952 (1960).

[13] D. R. Schultz and R. W. Parry, *J. Am. Chem. Soc.*, **80**, 4 (1958).

[14] R. A. Geanangel and S. G. Shore, "Preparative Inorganic Reactions," Vol. 3, Interscience Publishers, Inc., New York, N. Y., 1966, pp 123–238.

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).