

- (20) Under the conditions used here about 11% of the original  $(\text{CH}_3)_2\text{NPCl}_2$  was recovered unreacted. Depending on time and temperature this value varied from 0 to 25% of the amount used.
- (21) As pointed out in ref 16 an increase in the electron-releasing power of the R group of the ether facilitates ether cleavage. The isopropyl group is usually considered to be more electron releasing than the ethyl group.
- (22) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.
- (23) A. B. Burg and J. Slota, *J. Am. Chem. Soc.*, **80**, 1107 (1958).
- (24) H. J. Vetter, *Naturwissenschaften*, **51**, 240 (1964).
- (25) J. K. Ruff, *J. Am. Chem. Soc.*, **83**, 2835 (1961).
- (26) C. F. Farran, Ph.D. Dissertation, University of Michigan, Ann Arbor, Mich., 1966. Farran's high-resolution spectrum of *solid*  $(\text{CH}_3)_2\text{NPCl}_2$  and his assignments are as follows: 3000.8 s ( $\nu''_{\text{CH}_3}$ ), 2993.4 s ( $\nu''_{\text{CH}_3}$ ), 2942.4 s ( $\nu''_{\text{CH}_3}$ ), 2922 m ( $\nu'_{\text{CH}_3}$ ), 2900.4 s ( $\nu'_{\text{CH}_3}$ ), 2878.3 m and 2864.9 m, sh ( $\nu'_{\text{CH}_3}$ ), 2841.2 s (-), 2809.4 s and 2796.7 m ( $\nu'_{\text{CH}_3}$ ), 1991.2 w (1303 + 696), 1680.6 w (1303 + 392), 1487.2 s ( $\delta''_{\text{CH}_3}$ ), 1463.1 s and 1451.4 s ( $\delta''_{\text{CH}_3}$ ), 1443.2 sh (-), 1440.8 s ( $\delta_{\text{CH}_3}$ ), 1432.2 m ( $\delta'_{\text{CH}_3}$ ), 1429.3 m (-), 1402.0 s ( $\delta'_{\text{CH}_3}$ ), 1303.2 s and 1298.3 sh ( $\nu'_{\text{CN}}$ ), 1188.3 m (696 + 498), 1174.4 s ( $\rho'_{\text{CH}_3}$ ), 1138.6 w ( $\rho''_{\text{CH}_3}$ ), 1096.9 ms (-), 1065.7 s and 1063.9 s ( $\rho''_{\text{CH}_3}$ ), 1029.5 w (696 + 335), 984.4 vs ( $\nu'_{\text{CN}}$ ), 833.7 vw (498 + 335), 731 vw (393 + 335), 696.5 s ( $\nu'_{\text{PN}}$ ), 498.0 vs ( $\nu'_{\text{PCl}}$ ), 437.2 vs ( $\nu'_{\text{PCl}}$ ), 392.5 vs ( $\delta''_{\text{NC}_2}$ ), 335.2 s ( $\rho'_{\text{NC}_2}$ ), 292.6 w (-), 220.2 m ( $\tau''_{\text{PN}}$ ).
- (27) In an improved process developed by M. Thomas (Ph.D. Dissertation, University of Utah, Salt Lake City, Utah, 1975), it was found that a 15% excess of  $\text{AlCl}_3$  eliminated formation of any contaminating 2:1 adduct. The product can be purified by crystallization from  $\text{CH}_2\text{Cl}_2$  at  $-10^\circ\text{C}$ .
- (28) Not isolated or identified; may rearrange.

Contribution from the Departments of Chemistry, University of Michigan, Ann Arbor, Michigan 48104, and University of Utah, Salt Lake City, Utah 84112

## Structure of $[2((\text{CH}_3)_2\text{N})_2\text{PCl}]\cdot\text{AlCl}_3$ , $((\text{CH}_3)_2\text{N})_3\text{P}\cdot((\text{CH}_3)_2\text{N})_2\text{PCl}\cdot\text{AlCl}_3$ , and Related Species—Diphosphorus Cations

C. W. SCHULTZ and R. W. PARRY\*

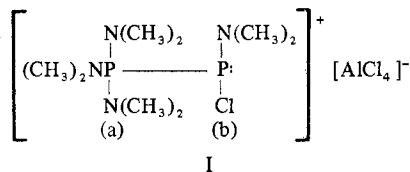
Received March 26, 1976

AIC60237D

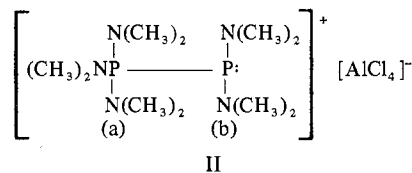
The bis-ligand adducts of  $\text{AlCl}_3$ ,  $[2((\text{CH}_3)_2\text{N})_2\text{PCl}]\cdot\text{AlCl}_3$  and  $((\text{CH}_3)_2\text{N})_3\text{P}\cdot((\text{CH}_3)_2\text{N})_2\text{PCl}\cdot\text{AlCl}_3$ , form easily but have been difficult to describe in conventional acid-base formalism since the analogous bis adduct containing 2 mol of  $((\text{CH}_3)_2\text{N})_3\text{P}$ /mol of  $\text{AlCl}_3$  could not be prepared. Structures of all pertinent compounds now provide an explanation. The compound  $[2((\text{CH}_3)_2\text{N})_2\text{PCl}]\cdot\text{AlCl}_3$  is shown to have the structure  $[((\text{CH}_3)_2\text{N})_3\text{P}-\text{P}(\text{N}(\text{CH}_3)_2)\text{Cl}]^+[\text{AlCl}_4]^-$ , while  $((\text{CH}_3)_2\text{N})_3\text{P}\cdot((\text{CH}_3)_2\text{N})_2\text{PCl}\cdot\text{AlCl}_3$  has the structure  $[((\text{CH}_3)_2\text{N})_3\text{P}-\text{P}(\text{N}(\text{CH}_3)_2)_2]^+[\text{AlCl}_4]^-$ . These conclusions are based on conductivity data, NMR spectra for  $^1\text{H}$  and  $^{31}\text{P}$  nuclei, infrared spectral data, and chemical information. The compound  $((\text{CH}_3)_2\text{N})_3\text{P}\cdot\text{AlCl}_3$  which will not add additional  $((\text{CH}_3)_2\text{N})_3\text{P}$  is shown to be a dimer with the initial structure  $[((\text{CH}_3)_2\text{N})_3\text{P}-\text{P}(\text{N}(\text{CH}_3)_2)_2]^+[\text{NR}_2(\text{AlCl}_3)_2]^-$ . The anion does not appear stable but undergoes further rearrangement. Apparent differences in chemistry are really due to the fact that the anion  $[\text{R}_2\text{NAlCl}_3]^+$  picks up a second mole of  $\text{AlCl}_3$  very easily. The  $[\text{GaCl}_4]^-$  and  $[\text{PF}_6]^-$  salts of the diphosphorus cation have been prepared, but we were not able to prepare  $[((\text{CH}_3)_2\text{N})_3\text{P}-\text{P}(\text{N}(\text{CH}_3)_2)\text{F}]^+$  in which a fluoride ion is coordinated to one phosphorus atom of the cation.

In the first paper of this series<sup>1</sup> interactions between (dimethylamido)chlorophosphorus(III) ligands and aluminum chloride were described. Conventional one to one addition compounds of the general formula  $((\text{CH}_3)_2\text{N})_n\text{Cl}_{3-n}\text{P}\cdot\text{AlCl}_3$  were reported along with two unexpected two to one addition compounds of formulas  $[2((\text{CH}_3)_2\text{N})_2\text{PCl}]\cdot\text{AlCl}_3$  and  $((\text{CH}_3)_2\text{N})_3\text{P}\cdot((\text{CH}_3)_2\text{N})_2\text{PCl}\cdot\text{AlCl}_3$ . Since both of these compounds were quite stable if air and water were excluded, it was particularly puzzling that no two to one addition compound involving the closely related  $((\text{CH}_3)_2\text{N})_3\text{P}$  and  $\text{AlCl}_3$  could be prepared. All attempts to prepare  $[2((\text{CH}_3)_3\text{N})_3\text{P}]\cdot\text{AlCl}_3$  have been singularly unsuccessful. Structural answers to correlate the foregoing facts are provided in this paper.

While the original structural questions seemed to center around the matter of a phosphorus-aluminum bond vs. a nitrogen-aluminum bond, it soon became clear that models based on either premise were unsatisfactory. In contrast, an ionic representation analogous to the cation  $[((\text{CH}_3)_3\text{P}-\text{P}(\text{CH}_3)_2)]^+$  reported by Noth<sup>2a</sup> and related species reported by Summers and Sisler<sup>2b</sup> gave a satisfactory representation of all observed properties. The compound  $[2((\text{CH}_3)_2\text{N})_2\text{PCl}]\cdot\text{AlCl}_3$  is best described by structural formula I. The related



compound  $((\text{CH}_3)_2\text{N})_3\text{P}\cdot((\text{CH}_3)_2\text{N})_2\text{PCl}\cdot\text{AlCl}_3$  is best described by structural formula II. The evidence to support



these assertions follows.

### Conductivity Data

If an ionic formulation is a proper representation of the foregoing compounds, solutions of each substance in methylene chloride should be electrical conductors. This expectation has been verified. A  $10^{-2}$  M solution of  $\text{AlCl}_3$  in methylene chloride has an equivalent conductance of  $0.21 \pm 0.01 \Omega^{-1} \text{cm}^2 \text{equiv}^{-1}$ . A comparable  $10^{-2}$  M solution of  $((\text{CH}_3)_2\text{N})_2\text{PCl}$  has an equivalent conductance of less than  $0.001 \Omega^{-1} \text{cm}^2 \text{equiv}^{-1}$ . On the other hand, a 0.3 M solution of  $[2((\text{C}-\text{H}_3)_2\text{N})_2\text{PCl}]\cdot\text{AlCl}_3$  has an equivalent conductance of  $22.2 \pm 0.3 \Omega^{-1} \text{cm}^2 \text{equiv}^{-1}$ . A simple ionic halide reference such as a 0.3 M solution of  $[(\text{C}_6\text{H}_5)_4\text{P}]\text{Cl}$  in methylene chloride gave a value of  $2.7 \pm 0.3 \Omega^{-1} \text{cm}^2 \text{equiv}^{-1}$ , and a reference covalent system such as  $\text{C}_6\text{H}_4\text{Br}_2$  gave a conductance of  $0.0008 \Omega^{-1} \text{cm}^2 \text{equiv}^{-1}$  under comparable conditions. Clearly an ionic representation is appropriate.<sup>3</sup>

In the first paper of this series<sup>1</sup> a molecular weight value of  $430 \pm 60$  was obtained from vapor pressure depression measurements in  $\text{CH}_2\text{Cl}_2$ , while a theoretical value of 443 was expected for  $[2((\text{CH}_3)_2\text{N})_2\text{PCl}]\cdot\text{AlCl}_3$ . The data would be consistent with a mildly dissociated ionic system (Structure I) in methylene chloride.

\* Author to whom correspondence should be addressed at the University of Utah.

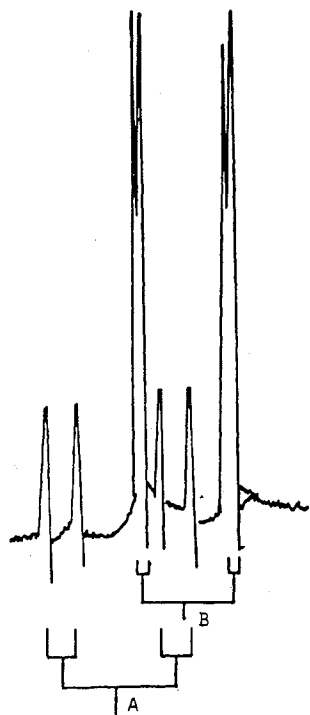


Figure 1. Proton NMR spectrum of  $[2((\text{CH}_3)_2\text{N})_2\text{PCl}]\cdot\text{AlCl}_3$  at 25 °C and 60 MHz: A, +2.34,  $J_{\text{PH}} = 12.0$  Hz,  $J_{\text{PPH}} = 3.4$  Hz; B, +2.42,  $J_{\text{PH}} = 9.2$  Hz,  $J_{\text{PPH}} = 0.6$  Hz.

#### Nuclear Magnetic Resonance Data

**<sup>1</sup>H NMR Spectrum of  $[2((\text{CH}_3)_2\text{N})_2\text{PCl}]\cdot\text{AlCl}_3$ .** For structure I assigned to this compound two hydrogen resonance peaks with an area ratio of 3:1 would be expected. Each of these peaks should be split into a doublet as a consequence of coupling with the phosphorus nucleus nearest to it; then each member of this doublet should be split further into a doublet by coupling with the remaining chemically nonequivalent phosphorus nucleus in the cation. The spectrum taken at ambient temperature and shown in Figure 1 is a textbook example of this behavior. Chemical shift values, referred to CH<sub>2</sub>Cl<sub>2</sub> as an internal standard, and coupling constants are easily obtained by first-order rules. For protons of total area 3,  $\delta$  is +2.46,  $J_{\text{PNCH}} = 9.3$  Hz, and  $J_{\text{PPNCH}} = 0.6$  Hz. For protons of area 1,  $\delta$  is 2.33,  $J_{\text{PNCH}} = 11.8$  Hz, and  $J_{\text{PPNCH}} = 3.4$  Hz. More detailed data including spectra in benzene are described elsewhere.<sup>4</sup> The proton data eliminate a structure containing an NR<sub>2</sub> bridge between phosphorus atoms.<sup>5</sup>

**<sup>31</sup>P NMR Spectrum of  $[2((\text{CH}_3)_2\text{N})_2\text{PCl}]\cdot\text{AlCl}_3$ .** For the cation formula in structure I two phosphorus resonances of equal intensity would be expected, since there are two chemically distinct phosphorus atoms. Each peak should be split into a doublet by its attached and nonequivalent phosphorus neighbor. Again the ambient-temperature spectrum in CH<sub>2</sub>Cl<sub>2</sub> is exactly that predicted. For the phosphorus atom containing three attached R<sub>2</sub>N groups (a in formula I),  $\delta$  is -50.2 from H<sub>3</sub>PO<sub>4</sub> and  $J_{\text{P-P}_a} = 352$  Hz. For the phosphorus atom containing one attached Cl<sup>-</sup> and one R<sub>2</sub>N<sup>-</sup> group (b in formula I),  $\delta$  is -118.2 from H<sub>3</sub>PO<sub>4</sub> and  $J_{\text{P-P}_b} = 352$  Hz. This value of the  $J_{\text{P-P}}$  coupling constant is very near the values frequently associated with a P-P bond,<sup>6a</sup> while the value of -50 for the chemical shift from 85% H<sub>3</sub>PO<sub>4</sub> is in the proper range for a four-coordinate phosphorus atom.<sup>6b</sup> Similarly the value of -119 is in the proper range for a three-coordinate phosphorus atom.

**<sup>1</sup>H NMR Spectrum of  $((\text{CH}_3)_2\text{N})_3\text{P}\cdot((\text{CH}_3)_2\text{N})_2\text{PCl}\cdot\text{AlCl}_3$ .** On the basis of the structure assigned to this species (formula

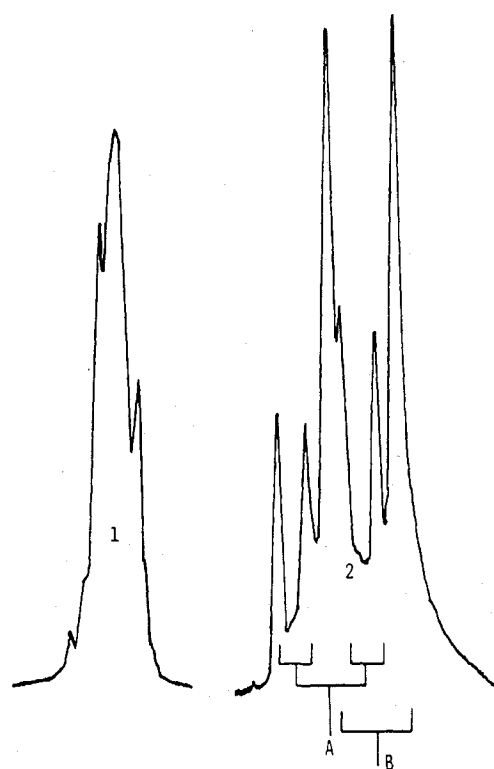
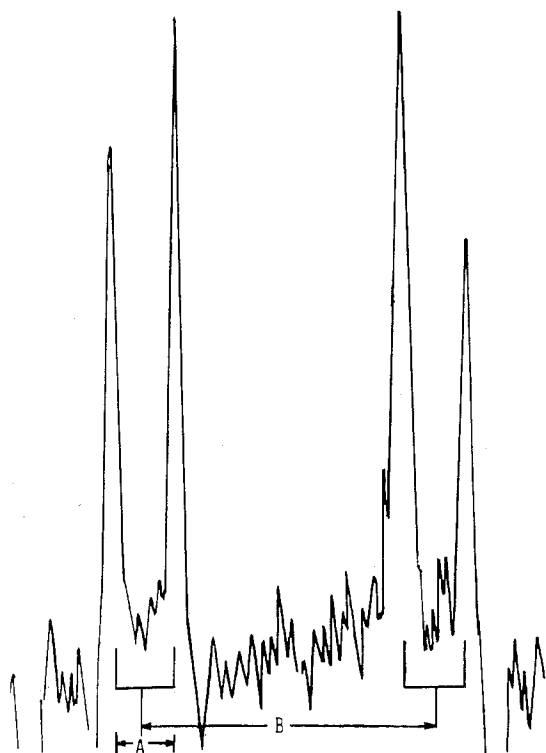


Figure 2. Proton NMR spectrum of  $((\text{CH}_3)_2\text{N})_3\text{P}\cdot((\text{CH}_3)_2\text{N})_2\text{PCl}\cdot\text{AlCl}_3$  (60-MHz instrument, CH<sub>2</sub>Cl<sub>2</sub> solvent): (1) ambient temperature; (2) -50 °C; A, +2.59,  $J_{\text{PH}} = 9.6$  Hz,  $J_{\text{PPH}} = 4.0$  Hz; B, +2.65,  $J_{\text{PH}} = 9.1$  Hz,  $J_{\text{PPH}}$  not measurable.

II) one would again anticipate two proton signals but with an area ratio of 3:2 rather than 3:1. Instead, the room-temperature <sup>1</sup>H spectrum consists of a broad singlet with fine peaks on each side of the central peak. See Figure 2. If a little extra ((CH<sub>3</sub>)<sub>2</sub>N)<sub>3</sub>P is added to the solution, the peak becomes a broad symmetrical singlet. On the other hand, cooling the original CH<sub>2</sub>Cl<sub>2</sub> solution to -50 °C produces the proton spectrum demanded by the model. A large doublet of area 3, assignable to the ((CH<sub>3</sub>)<sub>2</sub>N)<sub>3</sub>P unit (a in formula II), is seen at  $\delta$  2.65. The observed coupling constant  $J_{\text{PNCH}}$  is 9.1 Hz. Splitting by the second phosphorus,  $J_{\text{PPNCH}}$ , was too small to resolve in these studies. The smaller doublet of area 2, assignable to the ((CH<sub>3</sub>)<sub>2</sub>N)<sub>2</sub>P<sup>-</sup> unit (b in formula II) appears at a  $\delta$  value of 2.59 from CH<sub>2</sub>Cl<sub>2</sub>. The coupling constant  $J_{\text{PNCH}}$  was 9.6 Hz while  $J_{\text{PPNCH}}$  could now be measured as 4.0 Hz. Coupling is observed from the *four-coordinate* phosphorus atom to the more distant hydrogens attached indirectly to the three-coordinate phosphorus atom,  $J_{\text{P-P-N-C-H}}$ . The reverse coupling through a reverse path is not seen. Tetracoordinate phosphorus is known<sup>7</sup> to have a greater long-range coupling constant to a proton than does a tricoordinate phosphorus atom. The proton spectrum is consistent with a low-temperature structure showing a P-P linkage but not with a structure containing a PNP bridge linkage.<sup>5</sup>

It is clear from the temperature dependence of the spectrum that a rapid exchange process is occurring at room temperature. Such a process obliterates differences in (CH<sub>3</sub>)<sub>2</sub>N groups. It is further of significance that comparable exchange did not occur in the structure of formula I where a chloride was attached to one of the two phosphorus atoms. This dynamic exchange process is understood and will be considered in detail in a subsequent publication. The low-temperature proton spectrum as presented is in complete agreement with the ionic model proposed (formula II).



**Figure 3.**  $^{31}\text{P}$  NMR spectrum of  $((\text{CH}_3)_2\text{N})_3\text{P}((\text{CH}_3)_2\text{N})_2\text{PCl}\cdot\text{AlCl}_3$  ( $-50^\circ\text{C}$ , 40.4 MHz,  $\text{CH}_2\text{Cl}_2$  solvent):  $A = J = 340$  Hz;  $B = 2C - J = 1183$  Hz;  $C = 768$  Hz =  $1/2[(\delta(\text{H}))^2 + J^2]^{1/2}$ .  $\delta(\text{H})_{\text{calcd}} = 1506$  Hz = 37.2 ppm;  $\delta(\text{H})_{\text{obsd}} = 1551$  Hz = 38.4 ppm.

**$^{31}\text{P}$  NMR Spectrum of  $((\text{CH}_3)_2\text{N})_3\text{P}((\text{CH}_3)_2\text{N})_2\text{PCl}\cdot\text{AlCl}_3$ .** No  $^{31}\text{P}$  spectrum could be detected for this species at room temperature. Since proton spectra had indicated rapid exchange of  $\text{N}(\text{CH}_3)_2$  groups attached to phosphorus, the broadening of the  $^{31}\text{P}$  at room temperature was to be expected. Excessive broadening would cause disappearance of the signal. Since the proton spectra had indicated slowing of the exchange at low temperatures, one would anticipate a pair of doublets for the  $^{31}\text{P}$  spectrum at low temperature. The  $^{31}\text{P}$  spectrum of the compound at  $-50^\circ\text{C}$  is shown in Figure 3. A second-order AB type pattern is clearly recognizable. One must conclude that chemical shift differences between phosphorus atoms of structure II are comparable in size to the  $J_{\text{P-P}}$  coupling constant. In structure I the chemical shift difference between phosphorus atoms was larger than  $J_{\text{PP}}$  and a first-order spectrum was observed. It is easy to see that the two phosphorus atoms of structure II have a more nearly comparable chemical environment than do the two phosphorus atoms of structure I. On this basis, a smaller difference in chemical shift values is to be expected for structure II.

By use of standard techniques and signal shape, a more quantitative analysis of the  $-50^\circ\text{C}$  signal is possible.<sup>8</sup> A calculation<sup>4</sup> of the chemical shift between the two sets of doublets gave a value of 37.3. The observed value was 38.4. By use of the calculated chemical shift difference of 37.2, the ratio of line intensities between an inner and outer membrane of one of the doublets was calculated.<sup>9</sup> The calculated intensity ratio was 1.56. The measured value was identical.<sup>4</sup>

The change in the  $^{31}\text{P}$  spectrum with a change in temperature will be considered in a subsequent more detailed analysis of ion dynamics.

#### Infrared Spectral Data

**Infrared Spectrum of  $((\text{CH}_3)_2\text{N})_3\text{P}((\text{CH}_3)_2\text{N})_2\text{PCl}\cdot\text{AlCl}_3$ .** Structure II shown for this species is characterized by the presence of an  $\text{AlCl}_4^-$  ion of  $T_d$  symmetry and by a cation of

$C_s$  symmetry if rapid rotation around the P-P, N-P, and C-N bonds is assumed. While the cation spectrum may be complex, the anion spectrum is easy to analyze. The  $\text{AlCl}_4^-$  ion ( $T_d$  point group) should have nine normal modes which can be identified as  $A_1 + E + 2 F_2$ . All four vibrations are Raman active but only the 2  $F_2$  are infrared active. Three fundamentals for  $\text{AlCl}_4^-$  have been quite clearly assigned at 495, 352, and  $180\text{ cm}^{-1}$ . Only the peaks at 495 and  $180\text{ cm}^{-1}$  are infrared active with the  $495\text{-cm}^{-1}$  peak being the most intense. The fourth fundamental has been assigned at  $125\text{ cm}^{-1}$  but some uncertainty remains.<sup>10</sup> Since our measurements did not cover the far-infrared region (below  $300\text{ cm}^{-1}$ ) the peak at  $495\text{ cm}^{-1}$  would be the only absorption characteristic of  $\text{AlCl}_4^-$  which should appear. The complex  $((\text{CH}_3)_2\text{N})_3\text{P}((\text{CH}_3)_2\text{N})_2\text{PCl}\cdot\text{AlCl}_3$  has a strong and sharp absorption at  $495\text{ cm}^{-1}$  as expected. Unfortunately, the original  $((\text{CH}_3)_2\text{N})_2\text{PCl}$  has a  $\text{PCl}$  vibration which absorbs at about  $510\text{ cm}^{-1}$  and  $\text{Al}_2\text{Cl}_6$  has a moderately weak band at  $492\text{ cm}^{-1}$ . Thus while the appearance of a band at  $495\text{ cm}^{-1}$  does not prove the existence of the  $\text{AlCl}_4^-$ , the strength and sharpness of this band is most consistent with the presence of the  $\text{AlCl}_4^-$  ion.

The spectrum of the complex shows a very strong resemblance to that of the free ligand.<sup>1</sup> The only noteworthy frequency shift is an increase on complex formation of about  $20\text{ cm}^{-1}$  in the frequencies assigned to  $\text{CN}\cdots\text{P}$  vibrations ( $1280, 980, 960\text{ cm}^{-1}$ ). Such a change could be related to an increase in bond strength resulting from an involvement of the lone pair on the nitrogen in a  $\pi$  bond with the positively charged phosphorus cation. A general delocalization and increase in bond order across all three atoms would give the observed shift. Such arguments for the cation are far from definitive.

All of the foregoing arguments apply to  $[2((\text{CH}_3)_2\text{N})_2\text{PCl}\cdot\text{AlCl}_3]$  as well as to the mixed double adduct.

#### Some Chemical Consequences of Structure I for $[2((\text{CH}_3)_2\text{N})_2\text{PCl}\cdot\text{AlCl}_3]$

The above complex is sensitive to oxygen. When measured amounts of oxygen were bubbled into a  $\text{CH}_2\text{Cl}_2$  solution of the diadduct in an NMR tube at  $-45^\circ\text{C}$ , proton peaks characteristic of the complex disappeared and new peaks appeared. A plot of oxygen pressure vs. quantity of oxygen added showed a sharp break after 0.5 mol of  $\text{O}_2$  had been added to 1 mol of  $[2((\text{CH}_3)_2\text{N})_2\text{PCl}\cdot\text{AlCl}_3]$ . This result suggests initial oxidation of only one phosphorus atom of the complex at  $-45^\circ\text{C}$  followed by decomposition of the compound. When the system was allowed to warm to room temperature in the presence of some oxygen, some volatile products identified from  $^{31}\text{P}$  NMR as  $(\text{CH}_3)_2\text{NPCl}_2$  and  $((\text{CH}_3)_2\text{N})_2\text{PCl}$  were obtained. The nonvolatile products showed  $^{31}\text{P}$  NMR peaks at  $-31.2, -27.2,$  and  $-24.0$  from  $\text{H}_3\text{PO}_4$ . The expected product  $((\text{CH}_3)_2\text{N})_3\text{PO}$  has a peak at  $-24$  while  $((\text{CH}_3)_2\text{N})_2\text{P}(\text{O})\text{Cl}$  and  $(\text{CH}_3)_2\text{NP}(\text{O})\text{Cl}_2$  have peaks at  $-30$  and  $18$ , respectively. The compound  $((\text{C}-\text{H}_3)_2\text{N})_3\text{PO}$  would appear to be a product but the identity of other species is still not completely resolved.

#### Structural Conclusions for $[2((\text{CH}_3)_2\text{N})_2\text{PCl}\cdot\text{AlCl}_3]$ and $((\text{CH}_3)_2\text{N})_3\text{P}((\text{CH}_3)_2\text{N})_2\text{PCl}\cdot\text{AlCl}_3$

While no single piece of the structural evidence presented for the above compounds can be used to establish structures I and II with certainty, the total impact of all of the data leaves little reasonable doubt that structures I and II are the proper representations of these complexes.

#### The Structure of $((\text{CH}_3)_2\text{N})_3\text{P}\cdot\text{AlCl}_3$

The compound  $((\text{CH}_3)_2\text{N})_3\text{P}\cdot\text{AlCl}_3$  differs dramatically from the formally related  $((\text{CH}_3)_2\text{N})_2\text{PCl}\cdot\text{AlCl}_3$  in that the former compound will *not* pick up a second mole of  $((\text{C}-$

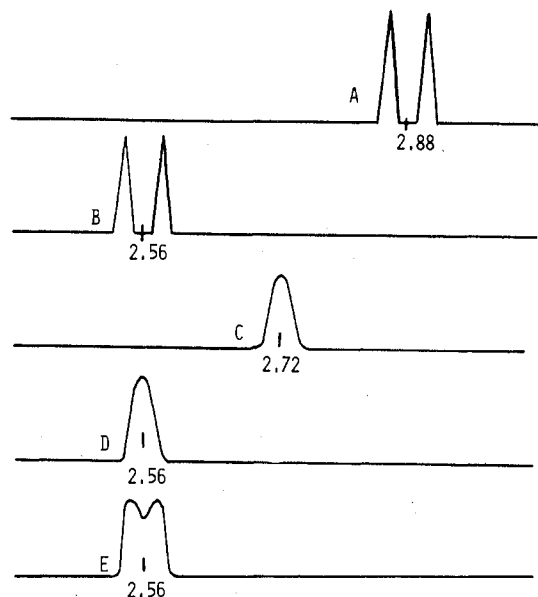
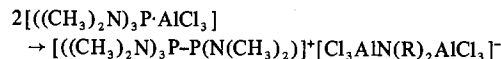


Figure 4. Proton NMR spectra of the system  $((\text{CH}_3)_2\text{N})_3\text{P}\cdot\text{AlCl}_3$  (25 °C, 60 MHz,  $\delta$  from  $\text{CH}_2\text{Cl}_2$ ): A,  $((\text{CH}_3)_2\text{N})_3\text{P}$  in  $\text{CH}_2\text{Cl}_2$ ; B,  $((\text{CH}_3)_2\text{N})_3\text{P}\cdot\text{AlCl}_3$  in  $\text{CH}_2\text{Cl}_2$ ; C,  $((\text{CH}_3)_2\text{N})_3\text{P}\cdot\text{AlCl}_3$  plus  $((\text{CH}_3)_2\text{N})_3\text{P}$  in  $\text{CH}_2\text{Cl}_2$ ; D,  $((\text{CH}_3)_2\text{N})_3\text{P}\cdot\text{AlCl}_3$ —solution C with excess  $((\text{CH}_3)_2\text{N})_3\text{P}$  removed (pumped on 1 day); E,  $((\text{CH}_3)_2\text{N})_3\text{P}\cdot\text{AlCl}_3$ —solution D with excess  $((\text{CH}_3)_2\text{N})_3\text{P}$  removed (pumped on 3 days).

$\text{H}_3)_2\text{N})_3\text{P}$  while the latter will pick up 1 mol of either  $((\text{CH}_3)_2\text{N})_3\text{P}$  or  $((\text{CH}_3)_2\text{N})_2\text{P}\text{Cl}$  to give the complexes represented by structures I and II. The fact is revealed clearly by a simple examination of the system. The complex  $((\text{CH}_3)_2\text{N})_2\text{P}\text{Cl}\cdot\text{AlCl}_3$  will dissolve in excess  $((\text{CH}_3)_2\text{N})_2\text{P}\text{Cl}$  to give a homogeneous system. In contrast, a system containing 2 mol of  $((\text{CH}_3)_2\text{N})_3\text{P}$  and 1 mol of  $\text{AlCl}_3$  consists of two phases: a liquid phase of excess  $((\text{CH}_3)_2\text{N})_3\text{P}$  and a solid phase of the one to one complex. When liquid  $\text{CH}_2\text{Cl}_2$  was added to the two-phase mixture, a clear colorless solution was obtained which could be used for proton NMR studies.

Figure 4A shows a diagrammatic representation of the 60-MHz proton spectrum of a 20% solution of  $((\text{CH}_3)_2\text{N})_3\text{P}$  in  $\text{CH}_2\text{Cl}_2$ . Figure 4B represents the comparable spectrum of the complex  $((\text{CH}_3)_2\text{N})_3\text{P}\cdot\text{AlCl}_3$ . Figure 4C represents the spectrum of the system containing 2 mol of  $((\text{CH}_3)_2\text{N})_3\text{P}$  and 1 mol of  $\text{AlCl}_3$  in  $\text{CH}_2\text{Cl}_2$  as a solvent. The collapsed *singlet* midway between the “doublets” seen for the free ligand and the one to one complex indicates that a rapid exchange process, probably involving cleavage of  $\text{P}\text{--}\text{N}$  bonds and exchange of  $\text{--}\text{NR}_2$  groups, will take place if both excess ligand and the one to one complex are present. After the spectrum indicated by Figure 4C had been taken, the volatile components were distilled from the system; then the solid residues were exposed to the vacuum pump for 24 h while the temperature of the solid was held at about 25 °C. After completion of this treatment the solid residues were dissolved in excess  $\text{CH}_2\text{Cl}_2$  and the NMR spectrum shown schematically in Figure 4D was obtained. Again removal of the solvent and exposure of the solid residues to the vacuum pumps for an additional 48 h, followed by redissolving of the solid in  $\text{CH}_2\text{Cl}_2$  and running of the  $^1\text{H}$  NMR spectrum at 25 °C, gave evidence of resolution of the single peak into two peaks, Figure 4E. The room-temperature spectrum of Figure 4D was identical with that of a  $\text{CH}_2\text{Cl}_2$  solution of  $((\text{CH}_3)_2\text{N})_3\text{P}\cdot\text{AlCl}_3$  containing a trace of excess  $((\text{CH}_3)_2\text{N})_3\text{P}$ . The foregoing observations indicate conclusively that a one to one complex of formula  $((\text{CH}_3)_2\text{N})_3\text{P}\cdot\text{AlCl}_3$  forms but no two to one complex. They further point up the difficulty in removing traces of excess ligand and show that traces of excess ligand promote exchange of  $\text{NR}_2$  groups.

Low-temperature NMR studies were clearly appropriate. The  $^1\text{H}$  and  $^{31}\text{P}$  spectra of  $((\text{CH}_3)_2\text{N})_3\text{P}\cdot\text{AlCl}_3$  at  $-57$  °C were identical with the comparable spectra obtained for  $[((\text{CH}_3)_2\text{N})_3\text{P}\text{--}\text{P}(\text{N}(\text{CH}_3)_2)_2]^+[\text{AlCl}_4]^-$  at the same temperature. When excess  $((\text{CH}_3)_2\text{N})_3\text{P}$  was present at  $-57$  °C, the signal for the free ligand could be clearly seen in both the  $^1\text{H}$  and  $^{31}\text{P}$  spectra. If one then writes the formula of the anion by difference, the following equation can be written



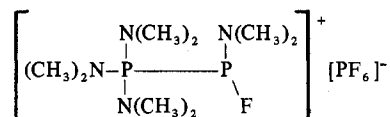
The difference in apparent behavior between  $((\text{CH}_3)_2\text{N})_3\text{P}\cdot\text{AlCl}_3$  and  $((\text{CH}_3)_2\text{N})_2\text{P}\text{Cl}\cdot\text{AlCl}_3$  must result from the fact that the anion  $[\text{Cl}_3\text{AlNR}_2]^-$ , presumably generated in complex formation, can pick up another  $\text{AlCl}_3$  group easily to give the bridged anion  $[\text{Cl}_3\text{AlN}(\text{R})_2\text{AlCl}_3]^-$  while the anion  $[\text{AlCl}_4]^-$  has a much smaller capability for picking up another  $\text{AlCl}_3$  group. The anion  $[\text{Cl}_3\text{AlN}(\text{R})_2\text{AlCl}_3]^-$  itself undergoes further decomposition at ambient temperature.<sup>11</sup>

These arguments then suggest that  $((\text{CH}_3)_2\text{N})_3\text{P}\cdot\text{AlBr}_3$  should behave as the corresponding aluminum chloride complex. The  $^1\text{H}$  NMR spectrum at low temperature indicated that the same cation was present in  $((\text{CH}_3)_2\text{N})_3\text{P}\cdot\text{AlBr}_3$ .

Because  $((\text{CH}_3)_2\text{N})_3\text{P}\cdot\text{AlCl}_3$  was insoluble in excess ligand yet dissolved in  $\text{CH}_2\text{Cl}_2$ , the possibility of a specific interaction with  $\text{CH}_2\text{Cl}_2$  to give a new compound involving one or more molecules of  $\text{CH}_2\text{Cl}_2$  remained. A tensimetric titration showed no specific interaction. The  $\text{CH}_2\text{Cl}_2$  served only as a solvent.<sup>4</sup>

#### Other Salts of the Cations $[((\text{CH}_3)_2\text{N})_3\text{P}\text{--}\text{P}(\text{N}(\text{CH}_3)_2)_2]^+$ and $[((\text{CH}_3)_2\text{N})_3\text{P}\text{--}\text{P}(\text{N}(\text{CH}_3)_2)_2\text{Cl}]^+$

When  $\text{GaCl}_3$  is allowed to react with an excess of  $((\text{C}\text{--}\text{H}_3)_2\text{N})_2\text{P}\text{Cl}$ , a compound is formed which can be assigned the formula  $[((\text{CH}_3)_2\text{N})_3\text{P}\text{--}\text{P}(\text{N}(\text{CH}_3)_2)_2\text{Cl}]^+[\text{GaCl}_4]^-$  on the basis of the proton NMR spectrum. Similarly the reaction of  $\text{PF}_5$  with an equimolar mixture of  $((\text{CH}_3)_2\text{N})_3\text{P}$  and  $((\text{CH}_3)_2\text{N})_2\text{PF}$  gave  $[((\text{CH}_3)_2\text{N})_3\text{P}\text{--}\text{P}(\text{N}(\text{CH}_3)_2)_2]^+[\text{PF}_6]^-$ , but we were *not* able to make the related compound



The reaction of  $\text{BCl}_3$  with  $((\text{CH}_3)_2\text{N})_2\text{P}\text{Cl}$  gave  $\text{Cl}_2\text{B}\text{--}\text{N}(\text{CH}_3)_2$  and  $\text{PCl}_3$  with *no* evidence for cation coordination. Direct initial formation of a  $\text{BN}$  bond rather than transfer of a  $\text{Cl}^-$  to  $\text{BCl}_3$  is suggested by the chemical observations.

#### Experimental Section

**General Data.** Compounds were prepared and reagents and compounds were purified and manipulated as described earlier.<sup>1</sup> Nuclear magnetic resonance spectra were obtained on a Varian HR-100 and on a Varian HA-60 spectrometer. Liquid  $\text{CH}_2\text{Cl}_2$ , dried over molecular sieves, was used as a solvent for compounds and as an internal standard for  $^1\text{H}$  spectra. A special reaction vessel was prepared with an attached 5-mm NMR tube.<sup>4</sup> By using this reactor, product could be transferred to the NMR tube without permitting exposure to air or water or a temperature rise above that used in compound preparation. The NMR tubes were then cooled to  $-196$  °C, evacuated, and sealed. In all operations extreme care was used to prevent exposure of materials to air or water. Aluminum chloride and aluminum bromide were sublimed under vacuum before use and always manipulated in a drybox or drybag with absolute minimum atmospheric contact. Gallium trichloride was prepared by burning gallium metal in a chlorine stream. The product was carefully sublimed before use and manipulated without access to air or water.

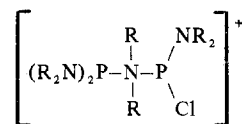
**Conductivity Measurements.** Great care was taken to avoid contamination of solutions with traces of moisture. A sealed cell was used in a standard Wheatstone bridge conductivity apparatus. The cell constant was  $0.1373 \text{ cm}^{-1}$ .

**Acknowledgment.** Support of this work by the National Institute of Health, Cancer Institute, through Grant CA 07989 to the University of Michigan and by the National Science Foundation through Grant GP 32079 to the University of Utah is gratefully acknowledged.

**Registry No.**  $[2((\text{CH}_3)_2\text{N})_2\text{P}(\text{Cl})\cdot\text{AlCl}_3]$ , 60594-85-6;  $((\text{CH}_3)_2\text{N})_3\text{P}\cdot((\text{CH}_3)_2\text{N})_2\text{P}(\text{Cl})\cdot\text{AlCl}_3$ , 60594-83-4;  $((\text{CH}_3)_2\text{N})_3\text{P}\cdot\text{AlCl}_3$ , 60594-91-4;  $^{31}\text{P}$ , 7723-14-0.

## References and Notes

- (1) R. W. Kopp, A. C. Bond, and R. W. Parry, *Inorg. Chem.* preceding paper in this issue.
- (2) (a) H. Noth, *Z. Naturforsch., B*, **15**, 327 (1960); (b) J. C. Summers and H. H. Sisler, *Inorg. Chem.*, **9**, 862 (1970).
- (3) Because conductance measurements in this system are extremely sensitive to traces of moisture, results are not of high precision, but they are sufficiently precise to establish the ionic nature of the product with a high degree of certainty.
- (4) C. W. Schultz, Ph.D. Dissertation, University of Michigan, Ann Arbor, Mich. 48104, 1969, pp 10-12.
- (5) One might write a model with a bridging  $\text{NR}_2$  group



Such a model should show three kinds of protons with area ratios of 2:1:1. Such was not observed.

- (6) (a) M. M. Crutchfield, C. H. Dugan, J. H. Letcher, V. Mark, and J. R. Van Wazer, *Top. Phosphorus Chem.*, **1**, 230 (1964); (b) *ibid.*, **1**, 49, 173-179 (1964); (c) *ibid.*, **5**, 230 (1967).
- (7) G. Mavel, *Prog. Nucl. Magn. Reson. Spectrosc.*, **1**, Chapter 4 (1966).
- (8) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance", McGraw-Hill, New York, N.Y., 1959, pp 119-123.
- (9) J. D. Roberts, "Nuclear Magnetic Resonance", McGraw-Hill, New York, N.Y., 1959, pp 55-56.
- (10) R. H. Bradley, P. N. Brier, and B. E. H. Jones, *J. Chem. Soc. A*, 1397 (1971).
- (11) A fairly detailed infrared study by J. Clements, M. G. Thomas, and R. W. Parry shows that the  $[\text{Cl}_3\text{AlNR}_2\text{AlCl}_3]^-$  ion itself undergoes decomposition to give  $[\text{Cl}_2\text{AlNR}_2]_n$  and  $\text{AlCl}_4^-$ . Results will be published separately.

Contribution from the Departments of Chemistry and Physics,  
Trinity College, Hartford, Connecticut 06106

## Preparation, Structure, and Properties of Ytterbium Ruthenium Hydride

ROBERT LINDSAY,\* RALPH O. MOYER, Jr.,\* JEFFERY S. THOMPSON, and DOUGLAS KUHN

Received April 16, 1976

AIC60285Y

$\text{Yb}_2\text{RuH}_6$ , a black polycrystalline solid, was formed by heating  $\text{YbH}_2$  and ruthenium powders at 800 °C in approximately 1 atm of hydrogen. X-ray powder diffraction data conformed to the face-centered cubic Bravais system, space group  $Fm\bar{3}m$ , with  $a = 7.248 \text{ \AA}$ . The structure was consistent with the metals arranged in a fluorite type lattice and in such a way that the ruthenium and ytterbium ions occupied the eight- and fourfold sites, respectively. The gram-susceptibility varied from about  $3 \times 10^{-6} \text{ emu/g}$  at room temperature to about  $8 \times 10^{-6} \text{ emu/g}$  at liquid  $\text{N}_2$  temperatures and departed from Curie-Weiss behavior in this region. Arguments are advanced showing that ytterbium and ruthenium in the ternary hydride are divalent. The electrical resistivity of  $\text{Yb}_2\text{RuH}_6$  was consistent with semiconductor behavior with  $\Delta E = 0.18 \text{ eV}$ .

### Introduction

Several investigations have been published drawing attention to the formation of some interesting ternary hydrides prepared by exposing binary alloys composed of lanthanum or a rare earth element and cobalt or nickel to hydrogen at or slightly above room temperature and at pressures above 1 atm. A particularly attractive feature of these alloys is their capacity to absorb large quantities of hydrogen. For example,  $\text{LaNi}_5\text{H}_{6.7}$  is formed by exposing  $\text{LaNi}_5$  to 2.5 atm of hydrogen at room temperature, and  $\text{SmCo}_5\text{H}_3$ , by the room-temperature hydrogen absorption of  $\text{SmCo}_5$  at 4.5 atm.<sup>1</sup>  $\text{DyCo}_3\text{H}_5$ ,  $\text{HoCo}_3\text{H}_5$ , and  $\text{ErCo}_3\text{H}_5$  are formed at room temperature by exposing the respective rare earth-cobalt alloys to hydrogen at 40 atm.<sup>2</sup> Our group, which is studying the formation, structure, and properties of rare earth-rarer platinum metal ternary hydrides, reported recently the formation of  $\text{Eu}_2\text{RuH}_6$ .<sup>3</sup> We wish to report now the results of our investigation of  $\text{Yb}_2\text{RuH}_6$ .<sup>4</sup>

### Experimental Section

Ytterbium ingot, presumably 99.9% pure, was purchased from A. D. MacKay, Inc., and from Electronic Space Products, Inc. The metal was purified further by vacuum distillation at 800 °C. In order to reduce the possibility of ferromagnetic contamination from the stainless steel distillation cold finger, the ytterbium was collected on a molybdenum disk, 0.005 in. thick, located at the tip of the cold finger. Ruthenium powder, 99.9% pure and 325 mesh, was purchased from A. D. MacKay, Inc. Prepurified grade hydrogen, purchased from

Airco Industries, Inc., was purified further by passing the gas through a hot palladium tube filter, Model A-1-DH, purchased from Matthey Bishop, Inc. Prepurified argon (99.998% minimum) and prepurified nitrogen (99.995%) were purchased from Airco Industrial Gases, Inc.

Distilled ytterbium was cut into chips, approximately  $1/4$  in. on edge and placed into a molybdenum boat, which in turn was loaded into a quartz reaction tube. The tube was attached to a glass vacuum line, and the system was evacuated to at least  $10^{-5}$  mm of mercury. Hydrogen was introduced into the system to approximately 700 mm of mercury, and the ytterbium was heated to 500 °C. The temperature was maintained at 500 °C for 4-5 h. Anal. Calcd for  $\text{YbH}_2$ : Yb, 98.85; H, 1.15. Found: Yb, 97.71; H, 1.12. X-ray powder diffraction data were consistent with the data published for ytterbium deuteride.<sup>5</sup>

Ytterbium ruthenium hydride was prepared by thoroughly mixing ytterbium hydride and ruthenium powders in a 2:1 mole ratio, respectively. A powdered mixture containing 0.7375 g of  $\text{YbH}_2$  and 0.2131 g of ruthenium was typical of the reactant size and was compressed at 5000 psi into a  $1/4$ -in. diameter pellet. The procedure for the high-temperature synthesis was similar to that reported elsewhere for  $\text{Eu}_2\text{RuH}_6$ .<sup>3</sup> The reactant pellet was heated at 800 °C for approximately 18 h in hydrogen at approximately 700 mm of mercury.

Elemental analyses of ytterbium and ruthenium were performed by gravimetric methods. Hydrogen was determined by thermal decomposition of the sample and its subsequent transfer to a calibrated gas buret. Procedures for the analyses are given elsewhere.<sup>3</sup>

Procedures for the x-ray diffraction, magnetic susceptibility, density, and electrical resistivity measurements have been reported elsewhere.<sup>3</sup> Deviations from these procedures are given below. X-ray powder diffraction intensities were determined by cutting the tracings above the background and weighing the paper on an analytical balance. Electrical resistivities were obtained from measurements on a pellet

\* To whom correspondence should be addressed: R. Lindsay, Department of Physics; R. O. Moyer, Jr., Department of Chemistry