(3) (a) See ref 2, Chapters 6–10; (b) *ibid.*, Chapter 9, pp 181, 190; also see p 143.
(4) J. K. Johanneson, *J. Chem. Soc.*, 2998 (1959).
(5) W. A. Brungs, *J. Water Pollut. Control Fed.*, **45**, 2180 (1973).
(6) J. D. Johnson and R. Overby, *J. Sanit. Eng. Div., Am. Soc. Civ. Eng.*, **97**, 617 (1970).
(7) H. Galal-Gorchev and J. C. Morris, *Inorg. Chem.*, **4**, 899 (1965).
(8) J. D. Johnson and R. Overby, *Anal. Chem.*, **41**, 1744 (1969).
(9) L. Farkas, M. Lewin, and R. J. Bloch, *J. Am. Chem. Soc.*, **71**, 1988 (1949).
(10) M. Lewin and M. Avrahami, *J. Am. Chem. Soc.*, **77**, 4491 (1955).
(11) P. Engel, A. Oplatka, and B. Perlmutter-Hayman, *J. Am. Chem. Soc.*, **76**, 2010 (1954).
(12) C. F. Prutton and S. H. Maron, *J. Am. Chem. Soc.*, **57**, 1652 (1935).
(13) H. A. Liebhafsky, and B. Makower, *J. Phys. Chem.*, **37**, 1037 (1933).
(14) "Standard Methods for the Examination of Water and Wastewater", 13th ed, American Public Health Association, Washington, D.C., 1971, pp 112–116.
(15) I. M. Kolthoff and R. Belcher, "Volumetric Analysis", Vol. 3, Interscience, New York, N.Y., 1957, pp 449–473.
(16) I. M. Kolthoff and J. J. Lingane, "Polarography", Vol. II, 2d ed, Interscience, New York, N.Y., 1952, p 946.
(17) I. M. Kolthoff and N. H. Furman, "Potentiometric Titrations: A Theoretical and Practical Treatise", Wiley, New York, N.Y., 1926.
(18) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis", Macmillan, New York, N.Y., 1946, p 557.
(19) C. M. Kelley and H. V. Tartar, *J. Am. Chem. Soc.*, **78**, 5752 (1956).

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Reactions of (Dimethylamido)halophosphorus(III) with Aluminum(III) Chloride and with Some Etherates of Aluminum(III) Chloride

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The chloro(dimethylamido)phosphorus(III) ligands interact with $AlCl_3$ under appropriate conditions to give $(CH_3)_2NPCl_2·AlCl_3$, $((CH_3)_2N)_2PCl·AlCl_3$, and $[2((CH_3)_2N)_2PCl]·AlCl_3$. Tris(dimethylamido)phosphorus(III) and $AlCl_3$ react under comparable conditions to give $((CH_3)_2N)_3P·AlCl_3$. The tris ligand will also react with $((CH_3)_2N)_2PCl·AlCl_3$ to give $((CH_3)_2N)_3P·((CH_3)_2N)_2PCl·AlCl_3$ but it will *not* react with $((CH_3)_2N)_3P·AlCl_3$ to give $[2((CH_3)_2N)_3P]·AlCl_3$. Trimethylamine will gradually replace some of the phosphorus ligand from the complex to give some $(CH_3)_3N·AlCl_3$. A solution of dichloro(dimethylamido)phosphorus(III) ligand in isopropyl ether was stable as was a solution of aluminum chloride in isopropyl ether. On the other hand, an isopropyl ether solution containing $AlCl_3$ *and* the dichloro(dimethylamido)phosphorus(III) ligand gave 1 mol of isopropyl chloride for each mole of PCl_3 and each mole of the dichloro(dimethylamido)phosphorus ligand. The ether solution turned red as a result of the formation of an aluminum chloride–olefin complex. The splitting process to generate alkyl halide was not observed with diethyl ether. The chloride transferred came from the phosphorus ligand, not the $AlCl_3$. The ligand $((CH_3)_2N)_2PCl$ will displace about 70% of the diisopropyl ether from the diisopropyl etherate of $AlCl_3$ and $((CH_3)_2N)_3P$ will displace 100% of the ether. Models to interpret these facts are presented.

The (dimethylamido)halophosphorus(III) ligands contain at least two quite different Lewis base centers. For example, the compound $((CH_3)_2N)_2PF$ contains *two* potentially basic nitrogen atoms and one potentially basic phosphorus atom. The site utilized in a given acid–base process is dependent upon the nature of the acid used. When borane fragments such as BH_3, B_3H_7, and B_4H_8 are used as the acid, bonding is known to be through the phosphorus atom.[1–5] When other boron acids such as BF_3, BCl_3, or $B(CH_3)_3$ are used, evidence indicates probable bonding through a nitrogen atom.[1–3,6,7] When aluminum alkyls are used as the acid, the behavior is more complicated. Clemens, Sisler, and Brey[8] studied the reaction of $(CH_3)_2NP(CH_3)_2$ with $Al(C_2H_5)_3$. They reported that a P–Al bond formed when the reagents were directly combined but that the structure changed to give an N–Al bond when the adduct was heated.

In this work the reactions of (dimethylamido)halophosphorus(III) ligands with $AlCl_3$ have been studied. Although it was originally assumed that a conventional acid–base adduct would be formed, structures and stoichiometry turned out to be quite different from those originally visualized.[9] In this paper the appropriate chemistry is summarized. Subsequent reports will probe questions of structure and molecular dynamics.

The System $(CH_3)_2NPF_2$–$AlCl_3$

Initial work with $(CH_3)_2NPF_2$ and $AlCl_3$ revealed a halogen-exchange process similar to that reported[10] for the system F_3P–$AlCl_3$. To eliminate complications resulting from halogen interchange to give AlF_3, the chloro ligand, $(CH_3)_2NPCl_2$, was used in place of its fluoro couterpart.

The System $(CH_3)_2NPCl_2$–$AlCl_3$

When excess $(CH_3)_2NPCl_2$ and $AlCl_3$ were directly combined at 20 °C in the vacuum system, the following reaction occurred almost quantitatively in 0.5 h or less

$$2(CH_3)_2NPCl_2 + AlCl_3 \rightarrow ((CH_3)_2N)_2PCl·AlCl_3 + PCl_3$$

Even at a temperature of −23 °C some PCl_3 formed as soon as the reactants were brought into contact. The foregoing observations were quite unexpected, since the equilibrium constant for the disproportionation of the *free ligand* to give $((CH_3)_2N)_2PCl$ and PCl_3 has been estimated as 5×10^{-4}, and according to Van Wazer and Maier,[11] an equimolar mixture of PCl_3 and $((CH_3)_2N)_2PCl$ undergoes essentially complete conversion to $(CH_3)_2NPCl_2$ in less than 30 s at 25 °C; PCl_3 is definitely not an expected product.

An application of simple mass law arguments to the equation for the reaction of $(CH_3)_2NPCl_2$ and $AlCl_3$ suggested the use of PCl_3 as a solvent to minimize PCl_3 formation and thus promote the formation of $(CH_3)_2PCl_2·AlCl_3$. Indeed, the monoadduct $(CH_3)_2NPCl_2·AlCl_3$ can be prepared from *equimolar* quantities of acid and base in PCl_3 at −23 °C, over a 12-h period. The pertinent equation is

$$(CH_3)_2NPCl_2 + AlCl_3 \xrightarrow[-23\ ^\circ\mathrm{C},\ 12\ \mathrm{h}]{PCl_3} (CH_3)_2NPCl_2·AlCl_3$$

The solid 1:1 adduct remaining after removal of the PCl_3 solvent undergoes disproportionation upon standing at 25 °C. The products are $((CH_3)_2N)_2PCl·AlCl_3$, PCl_3, and $AlCl_3$.

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About 20–30% of the relatively pure adduct was found to decompose in *8 days at 25 °C.* The solid also reacts rapidly at 25 °C with excess ligand

$$(CH_3)_2NPCl_2 \cdot AlCl_3 + (CH_3)_2NPCl_2 \rightarrow ((CH_3)_2N)_2PCl \cdot AlCl_3 + PCl_3$$

With trimethylamine a base displacement reaction occurs rapidly at 25 °C to give $(CH_3)_2NPCl_2$ and $(CH_3)_3N \cdot AlCl_3$.

The System $((CH_3)_2N)_2PCl$–$AlCl_3$

Direct combination of $((CH_3)_2N)_2PCl$ and $AlCl_3$ in a 1:1 mole ratio gives $((CH_3)_2N)_2PCl \cdot AlCl_3$ as a waxy solid which is identical in properties with the material prepared from $(CH_3)_2NPCl_2 \cdot AlCl_3$ and $(CH_3)_2NPCl_2$ as described above. Reaction of $((CH_3)_2N)_2PCl \cdot AlCl_3$ with trimethylamine gives $((CH_3)_2N)_2PCl$ and $(CH_3)_3N \cdot AlCl_3$ in a regular base displacement process.

In a completely unexpected process $((CH_3)_2N)_2PCl \cdot AlCl_3$ picks up a second mole of $((CH_3)_2N)_2PCl$ to give a stable 2:1 adduct $[2((CH_3)_2N)_2PCl] \cdot AlCl_3$. The compound $((CH_3)_2N)_2PCl \cdot AlCl_3$ will also pick up 1 mol of $((CH_3)_2N)_3P$ to give $((CH_3)_2N)_2PCl \cdot ((CH_3)_2N)_3P \cdot AlCl_3$. These complexes containing 2 mol of ligand/mol of $AlCl_3$ were originally formulated[9] as five-coordinate aluminum species by analogy to the known[12] structure of $((CH_3)_3N)_2 \cdot AlH_3$ and the proposed[8] structure for $((C_6H_5)_2P)_2N(C_2H_5) \cdot Al(C_2H_5)_3$ and related species. Subsequent work has eliminated the five-coordinate model in favor of an ionic one which is described in the accompanying paper.

Condensation of excess phosphorus(III) ligand onto a 2:1 adduct such as $[2((CH_3)_2N)_2PCl] \cdot AlCl_3$ simply dissolves the complex. The NMR spectrum showed distinct peaks for both the free and complexed ligand. No evidence for a 3:1 or higher adduct was found.

When PCl_3 is condensed onto $[2((CH_3)_2N)_2PCl] \cdot AlCl_3$, halogen–amido group exchange occurs as shown by

$$[2((CH_3)_2N)_2PCl] \cdot AlCl_3 + PCl_3 \rightarrow ((CH_3)_2N)_2PCl \cdot AlCl_3 + 2(CH_3)_2NPCl_2$$

The compound of composition $((CH_3)_2N)_3P \cdot ((CH_3)_2N)_2PCl \cdot AlCl_3$ fumes in moist air. It can be held at 65 °C for 3 days in the vacuum system with no evidence of decomposition. After 2 days at 98 °C in the vacuum system, $P(NR_2)_3$ is driven off leaving a yellow residue.

The System $((CH_3)_2N)_3P$–$AlCl_3$

An *excess* of $((CH_3)_2N)_3P$ reacts with $AlCl_3$ to give *only* a *one to one* adduct, $((CH_3)_2N)_3P \cdot AlCl_3$. *No evidence for a double adduct comparable to* $[2((CH_3)_2N)_2PCl] \cdot AlCl_3$ *was ever found.* This fact is very difficult to harmonize with the original five-coordinate aluminum model for $[2((CH_3)_2N)_2PCl] \cdot AlCl_3$ and was one of the key observations leading to new structural postulates.

Although $((CH_3)_2N)_3P \cdot AlCl_3$ will not pick up another mole of $((CH_3)_2N)_3P$, it *will* pick up 1 mol of $((CH_3)_2N)_2PCl$ to give the previously identified compound $((CH_3)_2N)_3P \cdot ((CH_3)_2N)_2PCl \cdot AlCl_3$. Addition of $(CH_3)_2NPCl_2$ to $((CH_3)_2N)_3P \cdot AlCl_3$ appears to give halogen–amido interchange since the product is $[2((CH_3)_2N)_2PCl] \cdot AlCl_3$. Similar halogen–amido interchange is noted when PCl_3 is added to $((CH_3)_2N)_3P \cdot AlCl_3$. The products recovered after 30 min are equimolar quantities of $(CH_3)_2N_2PCl \cdot AlCl_3$ and $(CH_3)_2NPCl_2$.

Reactions of the (Dimethylamido)halophosphorus(III) Ligands with Aluminum Chloride Etherates

In early attempts to prepare amidohalophosphorus(III) adducts of $AlCl_3$, diisopropyl ether was used as a solvent. Significant quantities of PCl_3 and isopropyl chloride were identified in the products. A solution of the (amido)halophosphorus(III) in isopropyl ether was stable under the conditions used, as was a solution of pure aluminum chloride in this ether. These facts prompted a more thorough study of the isopropyl etherate of aluminum chloride and of its exchange reactions with (dimethylamido)halophosphorus(III) ligands.

The Diisopropyl Etherate of Aluminum Chloride. The di-*n*-propyl etherate of $AlCl_3$ was first described as a red liquid in 1915,[13] but the diisopropyl etherate of $AlCl_3$ prepared in this study was a white solid which showed no decomposition over a 3-day period in the vacuum system at 25 °C. In the presence of a trace of water it changed in a matter of a few hours to a moist yellow solid. After a few days a red liquid covering a red-brown solid appeared. These observations can be understood on the basis of literature records. A trace of water hydrolyzes the AlCl bond to liberate HCl. The HCl then attacks the ether to give some isopropyl chloride. The resulting isopropyl chloride will split out HCl in the presence of $AlCl_3$,[14] to give unsaturated hydrocarbons which complex with the $AlCl_3$ to give a colored solution. The scarlet complex between $AlCl_3$ and an olefin was established by Burbage and Garrett,[15] who reported the evolution of HBr when liquid *n*-butyl bromide was added to $AlBr_3$. A scarlet liquid addition compound, 1-butene–aluminum bromide, was isolated and characterized by Burbage and Garrett.[15] Thus the development of color in the higher etherates of aluminum chloride is a fairly sensitive criterion for ether decomposition. Further discussion on the etherates of aluminum chloride is available elsewhere.[16–18]

Reaction of Phosphorus Trichloride with the Diisopropyl Etherate of Aluminum Chloride. Equimolar quantities of the diisopropyl etherate of $AlCl_3$ and PCl_3 were frozen at −196 °C and then warmed to 0 °C and held for 18 h in the vacuum line. The system turned red as expected. About a 1.07-mmol quantity of isopropyl chloride was separated for each millimole of PCl_3 used. When excess trimethylamine was added to the remaining product after removal of the R–Cl, 1 mol of $(CH_3)_3N$ was retained for each mole of $AlCl_3$ originally present, and $(CH_3)_2CHP(O)Cl_2$ was released. The latter compound had an infrared spectrum which was identical with the spectrum of an authentic sample.[19] Equations which describe the foregoing observations are

$$((CH_3)_2CH)_2O \cdot AlCl_3 + PCl_3 \rightarrow (CH_3)_2CHCl + (CH_3)_2CHOPCl_2 \cdot AlCl_3$$

$$(CH_3)_2CHOPCl_2 \cdot AlCl_3 + (CH_3)_3N \rightarrow (CH_3)_3N \cdot AlCl_3 + (CH_3)_2CHOPCl_2$$

$$(CH_3)_2CHOPCl_2 \xrightarrow[\text{Arbusov rearrangement}]{(CH_3)_2CHCl} (CH_3)_2CHP(O)Cl_2$$

Very nearly 1 mol of chloride is transferred per mole of PCl_3 used. The product $(CH_3)_2CHOPCl_2$ undergoes the expected Arbusov rearrangement in the presence of an alkyl halide. The red color of the product arises from the presence of the isopropyl chloride in the presence of $AlCl_3$ and the resulting generation of a small amount of red olefin–aluminum chloride complex. It is significant that no isopropyl ether was found in the products.

Reaction of (Dimethylamido)dichlorophosphorus(III) with the Diisopropyl Etherate of Aluminum Chloride. When $(CH_3)_2NPCl_2$ was allowed to react with the diisopropyl etherate of aluminum chloride under conditions comparable to those used for PCl_3 (except reaction time was 7 h),[19] nearly 1 mol of isopropyl chloride was formed for each mole of $(CH_3)_2NPCl_2$ used. Addition of excess $(CH_3)_3N$ to the products gave 1 mol of $(CH_3)_3N \cdot AlCl_3$ for each mole of $AlCl_3$ originally used. As expected, the products were red, but no attempt was made to isolate the other expected substance, $((CH_3)_2CHO)P(NR_2)Cl$, or its rearrangement product. The equations describing the foregoing observations are

$$((CH_3)_2CH)_2O\cdot AlCl_3 + (CH_3)_2NPCl_2 \rightarrow (CH_3)_2CHCl$$
$$+ (CH_3)_2CHOP(N(CH_3)_2)Cl\cdot AlCl_3$$

$$(CH_3)_2CHOP(N(CH_3)_2)Cl\cdot AlCl_3 + N(CH_3)_3$$
$$\rightarrow (CH_3)_3N\cdot AlCl_3 + [(CH_3)_2CHOP(N(CH_3)_2)Cl]^{28}$$

Reaction of Bis(dimethylamido)chlorophosphorus(III) with the Diisopropyl Etherate of Aluminum Chloride. As expected from the foregoing result, the use of $((CH_3)_2N)_2PCl$ with the diisopropyl etherate of aluminum chloride generated a very small amount of isopropyl chloride. About 70% of the original ether could be pumped slowly from the system, but evidence clearly suggested an unstable adduct involving the ether, the bis(dimethylamido)chlorophosphorus(III), and the aluminum chloride.

Reaction of Tris(dimethylamido)phosphorus(III) with the Diisopropyl Etherate of Aluminum Chloride. When $((CH_3)_2N)_3P$ was mixed with $((CH_3)_2CH)_2O\cdot AlCl_3$ in a 1:1 mole ratio at −196 °C, then warmed to 0 °C, and held at 0 °C for 5 h, complete displacement of the ether resulted. The other product was $((CH_3)_2N)_3P\cdot AlCl_3$. As expected, no isopropyl chloride could be detected and no color was observed in the system.

The foregoing process is a straightforward base displacement process and contrasts sharply with the chlorination process observed with $(CH_3)_2NPCl_2$ and with PCl_3. In view of the foregoing facts it is concluded that the chloride of the alkyl chloride comes from the P–Cl, not the $AlCl_3$.

Reaction of (Dimethylamido)chlorophosphorus(III) with the Diethyl Etherate of Aluminum Chloride. It is known that diisopropyl ether undergoes cleavage more easily than does diethyl ether;[21] thus the reaction of $(C_2H_5)_2O\cdot AlCl_3$ and $(CH_3)_2NPCl_2$ was of interest. When an equimolar, homogeneous mixture of $(C_2H_5)_2O\cdot AlCl_3$ and $(CH_3)_2NPCl_2$ was held at 0 °C for about 10 h and then fractionated, about 11% of the original ether was displaced and about 89% of the original phosphine was recovered. Only a trace of ethyl chloride was detected. As expected, the halide-transfer process is less facile with the diethyl etherate than with the diisopropyl etherate.

Experimental Section

General Procedures. Standard vacuum-line procedures[22] were used throughout. Storage tubes and reaction tubes were equipped with greaseless Fischer–Porter 4-mm Teflon needle valves and were connected to the vacuum system with O-ring joints. Apiezon grease was used on other glass valves. All solid materials were handled under dry N_2 in a drybox.

Molecular weight estimates were made by dissolving a known amount of the sample (about 300 mg) in a known amount of CH_2Cl_2 (about 8 g). Vapor pressure at 0 °C was measured.

Infrared spectra were taken on a Perkin-Elmer 337 grating spectrometer. For gases a cell with KBr windows was used. Liquids were run as films on a KBr plate; solids were run in a KBr pellet. Nuclear magnetic resonance data were obtained using a Varian A-60, or a Varian HR-100 spectrometer. Detailed spectra, which provided the basis for all structural assignments, will be presented in the following paper.

Starting Materials. Commercial $AlCl_3$ (Baker and Adamson reagent grade) was purified by multiple sublimation in a stream of dry nitrogen. Malinckrodt reagent grade PCl_3 was condensed onto dry $AlCl_3$ and then fractionated through traps at −45, −83, and −196 °C. The −83 °C fraction was used. The $(CH_3)_3N$ was generated from $(CH_3)_3NHCl$ (Eastman) using 50% NaOH. The material was passed through a −83 °C trap into a −196 °C trap. The −196 °C fraction was used. Commercial reagent grade ethers were dried over CaH_2. Methylene chloride was stored over Drierite. The $(CH_3)_2NPCl_2$ was prepared by adapting the procedure of Burg and Slota[23] to vacuum-line techniques. Details are available elsewhere.[9] The $((CH_3)_2N)_3P$ was prepared by an adaptation[9] of the method of Holmes and Wagner.[6] The $((CH_3)_2N)_2PCl$ was prepared by combining 2 mol of $((CH_3)_2N)_3P$ with 1 mol of PCl_3 in the vacuum system at −196 °C. After warming of the mixture to 25 °C with stirring, the pure product (as determined by NMR: $\delta(^1H)$ −2.65 (TMS),[24] J_{PNCH} = 12.1 Hz;[24] $\delta(^{31}P)$ −160 (H_3PO_4)[25]) was obtained.

Reaction of Neat $(CH_3)_2NPCl_2$ with $AlCl_3$—Synthesis of $((CH_3)_2N)_2PCl\cdot AlCl_3$ and PCl_3. A typical reaction out of many is described. A 5.15-mmol sample of $(CH_3)_2NPCl_2$ was condensed onto 1.09 mmol of pure dry $AlCl_3$ in the vacuum system at −196 °C. The reaction vessel and contents were then warmed to 0 °C and held for 20 h with occasional stirring. Fractionation of the volatile components gave 2.91 mmol of unreacted $(CH_3)_2NPCl_2$ and 1.06 mmol of PCl_3. The waxy, water-sensitive solid remaining in the tube (mp 60–65 °C) had the overall formula $((CH_3)_2N)_2PCl\cdot AlCl_3$. The detailed characterization of the compound is given under the description of the reaction of $((CH_3)_2N)_2PCl$ and $AlCl_3$. In separate studies to determine rate of the reaction it was found that an equilibrium pressure of PCl_3 was reached after 25 min at 25 °C.

Reaction of $(CH_3)_2NPCl_2$ with $AlCl_3$ Dissolved in PCl_3—Synthesis of $(CH_3)_2NPCl_2\cdot AlCl_3$. In one run a 2.67-mmol sample of $AlCl_3$ was suspended in 6.530 g (47.51 mmol) of PCl_3. A 2.53-mmol sample of $(CH_3)_2NPCl_2$ was frozen at −196 °C above the $AlCl_3$–PCl_3 mixture. The system was warmed to −20 °C and held there for 9 h with occasional stirring. Fractionation of the volatiles pulled from the tube at −20 °C (−45 and −196 °C traps) produced 47.59 mmol of PCl_3 (−196 °C) and 0.28 mmol of $(CH_3)_2NPCl_2$ (−45 °C). When the system was warmed to room temperature, the product was a clear, fairly mobile liquid, perhaps from solvent PCl_3 generated by decomposition of the original product. As this liquid stood for 8 days, more PCl_3 was generated. An 0.44-mmol sample of PCl_3 was pulled from the system. The product $(CH_3)_2NPCl_2\cdot AlCl_3$ is clearly unstable and converts readily to $((CH_3)_2N)_2PCl\cdot AlCl_3$ and PCl_3. This instability proved to be somewhat of a problem in studying the dichloro(dimethylamido)phosphorus(III)–aluminum chloride complex, but, as will be noted later, its decomposition could be followed and interpreted by use of NMR spectroscopy.

When an excess of $N(CH_3)_3$ (5.40 mmol) was condensed onto a 2.60-mmol sample of slowly decomposing $(CH_3)_2NPCl_2\cdot AlCl_3$ and the entire system was held for 18 h at 0 °C, volatile materials were obtained. Identified were 2.09 mmol of $N(CH_3)_3$ and 1.61 mmol of $(CH_3)_2NPCl_2$. The above facts suggest that about 60% of the original (dimethylamido)dichlorophosphorus(III) was displaced from the complex. The infrared spectra of the free ligand and the complex are summarized here. Assignments for the ligand are essentially those of Farran.[26] The order used is as follows: frequency in cm^{-1}, intensity (s = strong, w = weak, m = medium, v = very, sh = shoulder), and probable assignment (with ν = stretch, ρ = rock, δ = deformation). While the spectrum of the gaseous ligand is compared here to the spectrum of the solid complex, Farran's[26] comparison of the spectra of solid and gaseous $(CH_3)_2NPCl_2$ indicates that a comparison of gas and solid at this level of resolution is appropriate. As expected, the solid spectrum has additional lines. The spectrum for gaseous $(CH_3)_2NPCl_2$ is as follows: 2980 sh (ν_{CH_3}), 2935 m (ν_{CH_3}), 2860 sh (ν_{CH_3}), 2810 mw (ν_{CH_3}), 1480 m (δ_{CH_3}), 1460 m (δ_{CH_3}), 1290 m (ν_{CNP}), 1187 m (ρ_{CH_3}), 1144 w (ρ_{CH_3}), 1068 mw (ρ_{CH_3}), 981 s (ν_{CNP}), 688 ms (ν_{NP}), 530 ms (ν_{PCl}), 508 vs (ν_{PCl}), 456 s (ν_{PCl}). For the solid complex $(CH_3)_2NPCl_2\cdot AlCl_3$, the spectrum is as follows: 2960 sh (ν_{CH_3}), 2940 m (ν_{CH_3}), 2800 w (ν_{CH_3}), 1475 sh (δ_{CH_3}), 1450 m (δ_{CH_3}), 1410 sh (–), 1295 ms (ν_{CNP}), 1172 ms (ρ_{CH_3}), 1057 m (ρ_{CH_3}), 1009 sh (ν_{CNP}), 984 vs (ν_{CNP}), 860 w (–), 805 w (–), 712 mw, (ν_{NP}), 690 m (ν_{NP}), 641 m (–), 585 m, sh (ν_{PCl}), 500 vs (AlCl), 430 m, sh (–).

Reaction of $((CH_3)_2N)_2PCl$ with $AlCl_3$—Synthesis of $((CH_3)_2N)_2PCl\cdot AlCl_3$. Equimolar amounts of resublimed $AlCl_3$ and $((CH_3)_2N)_2PCl$ were combined in the vacuum line using previously described techniques. A waxy solid formed.[27] The molecular weight of the product as measured by vapor pressure depression of CH_2Cl_2 at 0 °C was 265 ± 35. The theoretical value for a monomer is 289. Additional characterization data are discussed under "structure" in a subsequent paper.

The principal infrared frequencies of the free ligand were recorded by three separate investigators. Kopp recorded those of the neat liquid, Schultz recorded those of a CH_2Cl_2 solution, and Thomas recorded those of the liquid. In no case did the different spectra differ by more than ten wavenumbers. Lines were usually closer. The best values are summarized here using the same notation scheme that was outlined in the preceding section: 3000 w (ν_{CH_3}), 2935 s (ν_{CH_3}), 2900 s (ν_{CH_3}), 2845 m sh (ν_{CH_3}), 2805 m (ν_{CH_3}), 1480 ms (δ_{CH_3}), 1450 s (δ_{CH_3}), 1410 w sh (δ_{CH_3}), 1280 s (ν_{CNP}), 1194 s (ρ_{CH_3}), 1160 sh (–), 1140 w (ρ_{CH_3}), 1095 vw (–), 1062 m (ρ_{CH_3}), 980 sh (ν_{CNP}), 960 vs (ν_{CNP}), 880 mw (–), 790 w (–), 700 ms (ν_{PN}), 672 m (ν_{PN}), 510 sh (ν_{PCl}), 490 m (ν_{PCl}), 410 w (δ_{CNC}), 307 w (–).

For the solid complex $((CH_3)_2N)_2PCl{\cdot}AlCl_3$ the frequencies and assignments are as follows: 2930 s (ν_{CH_3}), 2815 m (ν_{CH_3}), 2420 w (–), 1585 w (–), 1475 sh and 1450 s (δ_{CH_3}), 1410 w (δ_{CH_3}), 1309 s (ν_{CNP}), 1220 sh (ν_{CNP}), 1186 s (ρ_{CH_3}), 1135 sh (–), 1003 sh (ν_{CNP}), 996 vs (ν_{CNP}), 805 w (combn), 733 w (combn), 710 vw (ν_{PN}), 620 w (ν_{PN}), 495 vs (ν_{AlCl}), 437 w, sh (δ_{CNC}).

Reaction of $((CH_3)_2N)_2PCl$ with $((CH_3)_2N)_2PCl{\cdot}AlCl_3$—Synthesis of the Diadduct $[2((CH_3)_2N)_2PCl]{\cdot}AlCl_3$. If an excess of $((CH_3)_2N)_2PCl$ (3.83 mmol) is condensed onto pure $AlCl_3$ (0.78 mmol) and allowed to react at 0 °C for 18 h as previously described, the ratio of ligand to $AlCl_3$ can be reduced to 2.15:1 by exposing the reaction vessel to the vacuum pumps. By flooding the product with hexane and pumping it off several times, we can reduce the ratio to 2.06:1. A pure product can be obtained by carefully combining the reagents in a 2:1 ratio.

The solid white product melts over the range 118–123 °C; it is soluble in methylene chloride and reacts vigorously with water vapor and almost explosively with liquid water. It has low solubility in benzene, hexane, chloroform, bromoform, and carbon tetrachloride. It molecular weight as determined by vapor pressure depression of CH_2Cl_2 at 0 °C was 430 ± 60. A monomer would have the theoretical value of 443. The infrared spectrum of the solid 2:1 adduct $[2((CH_3)_2N)_2PCl]{\cdot}AlCl_3$ is given here using the same notation as that used in the preceding section: 2935 ms (ν_{CH_3}), 2900 m (ν_{CH_3}), 2850 w (ν_{CH_3}), 2810 mw (ν_{CH_3}), 1475 m sh (δ_{CH_3}), 1455 m (δ_{CH_3}), 1410 w sh (δ_{CH_3}), 1300 s (ν_{CNP}), 1170 s (ρ_{CH_3}), 1140 w (ρ_{CH_3}), 1062 s (ρ_{CH_3}), 1008 s sh (ν_{CNP}), 984 vs (ν_{CNP}), 745 mw (–), 692 w (ν_{NP}), 668 m (ν_{NP}), 490 vs (ν_{AlCl}), 437 w (δ_{CNC}).

Reactions of $((CH_3)_2N)_2PCl{\cdot}AlCl_3$ with Various Reagents—Synthesis of $((CH_3)_2N)_2PCl{\cdot}((CH_3)_2N)_3P{\cdot}AlCl_3$. In general, reagents were condensed onto a sample of $((CH_3)_2N)_2PCl{\cdot}AlCl_3$ in the vacuum system at −196 °C. The temperature was raised to 0 °C and held for periods ranging from hours up to 5 days. Volatile materials were then removed at 0 °C and fractionated.

An excess of trimethylamine displaced less than half of the ligand in a single exposure. Removal of volatile materials followed by reexposure to the amine permitted recovery of up to 68% of the original $((CH_3)_2N)_2PCl$ in the complex.

A fourfold molar excess of $((CH_3)_2N)_3P$ was allowed to stand 5 days on the complex at 25 °C. When excess $((CH_3)_2N)_3P$ was pumped off, 1.07 mol of $((CH_3)_2N)_3P$ was retained for each mole of complex used.

Reaction of $((CN_3)_2N)_3P$ with $AlCl_3$. In a typical run carried out as described earlier, a 2.11-mmol sample of $AlCl_3$ reacted with 2.19 mmol of $((CH_3)_2N)_3P$. The complex appeared as an insoluble precipitate in liquid ligand if excess ligand were used. The adduct melted at 105–112 °C and then decomposed to a dark brown solid. The molecular weight of the solid in methylene chloride (mole fraction of solute 0.127) at 0 °C was 320 ± 50. The theoretical value for a monomer is 297.5. *It was of special significance that no evidence for a complex with 2 mol of ligand/mol of $AlCl_3$ was ever found.* Reaction of the complex with $((CH_3)_2N)_2PCl$ gave the previously described double adduct: $((CH_3)_2N)_3P{\cdot}((CH_3)_2N)_2PCl{\cdot}AlCl_3$.

Condensation of a 3.00-mmol sample of $(CH_3)_2NPCl_2$ onto 1.22 mmol of $((CH_3)_2N)_3P{\cdot}AlCl_3$ at −196 °C followed by warming to room temperature gave evidence for the absorption of 1.12 mmol of $(CH_3)_2NPCl_2$. The facts are best summarized by the equation

$$((CH_3)_2N)_3P{\cdot}AlCl_3 + (CH_3)_2NPCl_2 \rightarrow [2((CH_3)_2N)_2PCl]{\cdot}AlCl_3$$

When a large excess of PCl_3 (32.98 mmol) was condensed as before onto a 2.11-mmol sample of $((CH_3)_2N)_3P{\cdot}AlCl_3$, two liquid layers were visible about 30 min after the system had been warmed to room temperature. After 3 days fractionation of volatile products gave 1.76 mmol of $(CH_3)_2NPCl_2$ and 30.98 mmol of PCl_3. The best equation to summarize these facts is

$$((CH_3)_2N)_3P{\cdot}AlCl_3 + PCl_3 \rightarrow ((CH_3)_2N)_2PCl{\cdot}AlCl_3 + (CH_3)_2NPCl_2$$

Reaction of $AlCl_3$ with Isopropyl Ether. A 37.96-mmol sample of isopropyl ether was condensed at −196 °C onto a 1.45-mmol sample of $AlCl_3$. The system was warmed to 25 °C and the resulting suspension was stirred for 6 h. When excess ether was removed, a 1.45-mmol sample of $AlCl_3$ retained a 1.45-mmol quantity of ether. The resulting dry white solid was stable for at least 3 days at room temperature. No evidence of isopropyl chloride or red color was found if reagents and system were scrupulously clean and dry.

Table I. Reaction of the Diisopropyl Etherate of $AlCl_3$ with $((CH_3)_2N)_nPCl_{3-n}$ (n = 0–3)

	Amt, mmol				
Ligand used	Ligand	Etherate	Time,[a] h	RCl: complex	Ether: complex
PCl_2	3.14	3.10	18	1.07	Trace
$(CH_3)_2NPCl_2$	7.81	7.87	7	1.0	Small amt[19]
$((CH_3)_2N)_2PCl$	3.63	3.53	18	Small amt	0.69
$((CH_3)_2N)_3P$	1.53	1.52	5	0	1.0

[a] In all cases reagents were mixed at −196 °C and warmed to 0 °C, where temperature was held for the time indicated.
[b] Treatment of the residue with $(CH_3)_3N$ resulted in pickup of 1 mol of $(CH_3)_3N$/mol of $AlCl_3$ and release of $((CH_3)_2CH)P(O)Cl_2$ as determined by infrared analysis.

Reaction of $((CH_3)_2CH)_2O{\cdot}AlCl_3$ with $((CH_3)_2N)_nPCl_{3-n}$ n = 0–3). All reactions were carried out as described above. Results are summarized in Table I.

Reaction of $(CH_3)_2NPF_2$ with $AlCl_3$. When $(CH_3)_2NPF_2$ and $AlCl_3$ were mixed with a slight excess of ligand, a complex process occurred. About two-thirds of the $(CH_3)_2NPF_2$ appeared as $(CH_3)_2NPCl_2$ and one-sixth as PF_3. In a typical run a 1.59-mmol sample of $AlCl_3$ and a 0.37-mmol sample of $(CH_3)_2NPF_2$ were condensed in the vacuum line at −23 °C. After 15 min the reaction mixture could not be condensed at −80 °C indicating the presence of PF_3. A total of 3.69 mmol of $(CH_3)_2NPF_2$ was added in three increments at −23 °C over a period of about 1 h; then the mixture stood for about 4 h at −23 °C. Fractionation of the products indicated that for 1.59 mmol of $AlCl_3$, 2.175 mmol of $(CH_3)_2NPF_2$ was consumed. A 1.369-mmol sample of $(CH_3)_2NPCl_2$ and a 0.24-mmol sample of PF_3 were obtained.

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Registry No. $((CH_3)_2N)_2PCl{\cdot}AlCl_3$, 60607-14-9; $(CH_3)_2NPCl_2{\cdot}AlCl_3$, 60594-92-5; $[2((CH_3)_2N)_2PCl]{\cdot}AlCl_3$, 60594-85-6; $((CH_3)_2N)_2PCl{\cdot}((CH_3)_2N)_3P{\cdot}AlCl_3$, 60594-83-4; $((CH_3)_2N)_3P{\cdot}AlCl_3$, 60594-91-4; $((CH_3)_2CH)_2O{\cdot}AlCl_3$, 18785-84-7; $(CH_3)_2NPCl_2$, 683-85-2; $AlCl_3$, 7446-70-0; $((CH_3)_2N)_2PCl$, 3348-44-5; $(CH_3)_2NPF_2$, 814-97-1; PCl_3, 7719-12-2.

References and Notes

(1) (a) S. Fleming, Ph.D. Dissertation, University of Michigan, Ann Arbor, Mich., 1963; (b) S. Fleming and R. W. Parry, *Inorg. Chem.*, **11**, 1 (1972).
(2) M. D. LaPrade and C. E. Nordman, *Inorg. Chem.*, **8**, 1669 (1969).
(3) H. Nöth and H. J. Vetter, *Chem. Ber.*, **96**, 1298 (1963).
(4) R. G. Cavell, *J. Chem. Soc.*, 1992 (1964).
(5) T. Reetz and B. Katlafsky, *J. Am. Chem. Soc.*, **82**, 5036 (1960).
(6) R. H. Holmes and R. R. Wagner, *J. Am. Chem. Soc.*, **84**, 357 (1962).
(7) The existence of a B–N bond is less certain than the existence of the B–P bond, but data are still fairly convincing.
(8) D. F. Clemens, H. H. Sisler, and W. S. Brey, *Inorg. Chem.*, **5**, 526 (1966).
(9) R. W. Kopp, Ph.D. Dissertation, University of Michigan, Ann Arbor, Mich., 1966.
(10) E. R. Alton, R. G. Montemayor, and R. W. Parry, *Inorg. Chem.*, **13**, 2267 (1974).
(11) J. R. Van Wazer and L. Maier, *J. Am. Chem. Soc.*, **86**, 811 (1964).
(12) C. W. Heitsch, C. E. Nordman, and R. W. Parry, *Inorg. Chem.*, **2**, 508 (1963).
(13) G. B. Frankforter and E. A. Daniels, *J. Am. Chem. Soc.*, **37**, 2560 (1915).
(14) E. Wertyporoch and T. Firla, *Z. Phys. Chem., Abt. A*, **162**, 398 (1932).
(15) J. J. Burbage and A. B. Garrett, *J. Phys. Chem.*, **56**, 730 (1952).
(16) F. Johnson, "Friedel-Crafts and Related Reactions", Vol. 4, G. Olah, Ed., Interscience, New Yoork, N.Y., 1963.
(17) G. Urry, "The Chemistry of Boron and Its Compounds", E. Muetterties, Ed., Wiley, New York, N.Y., 1967, p 332.
(18) P. Hagenmuller and J. Rauxel, *C. R. Hebd. Seances Acad. Sci.*, **247** (1958).
(19) A. M. Kinnear and E. A. Perren, *J. Chem. Soc.*, 3437 (1952); L. J. Bellamy, "The Infra-red Spectra of Complex Molecules", Wiley, New York, N.Y., 1957, p 314.

(20) Under the conditions used here about 11% of the original $(CH_3)_2NPCl_2$ 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* $(CH_3)_2NPCl_2$ and his assignments are as follows: 3000.8 s (ν''_{CH_3}), 2993.4 s (ν''_{CH_3}), 2942.4 s (ν''_{CH_3}), 2922 m (ν'_{CH_3}), 2900.4 s (ν'_{CH_3}), 2878.3 m and 2864.9 m, sh (ν'_{CH_3}), 2841.2 s (–), 2809.4 s and 2796.7 m (ν'_{CH_3}), 1991.2 w (1303 + 696), 1680.6 w (1303 + 392), 1487.2 s (δ''_{CH_3}), 1463.1 s and 1451.4 s (δ''_{CH_3}), 1443.2 sh (–), 1440.8 s (δ_{CH_3}), 1432.2 m (δ'_{CH_3}), 1429.3 m (–), 1402.0 s (δ'_{CH_3}), 1303.2 s and 1298.3 sh (ν'_{CN}), 1188.3 m (696 + 498), 1174.4 s (ρ'_{CH_3}), 1138.6 w (ρ''_{CH_3}), 1096.9 ms (–), 1065.7 s and 1063.9 s (ρ''_{CH_3}), 1029.5 w (696 + 335), 984.4 vs (ν'_{CN}), 833.7 vw (498 + 335), 731 vw (393 + 335), 696.5 s (ν'_{PN}), 498.0 vs (ν'_{PCl}), 437.2 vs (ν''_{PCl}), 392.5 vs (δ''_{NC_2}), 335.2 s (ρ'_{NC_2}), 292.6 w (–), 220.2 m (T″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 $AlCl_3$ eliminated formation of any contaminating 2:1 adduct. The product can be purified by crystallization from CH_2Cl_2 at −10 °C.

(28) Not isolated or identified; may rearrange.

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Structure of $[2((CH_3)_2N)_2PCl]\cdot AlCl_3$, $((CH_3)_2N)_3P\cdot((CH_3)_2N)_2PCl\cdot AlCl_3$, and Related Species—Diphosphorus Cations

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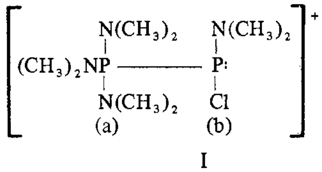
The bis-ligand adducts of $AlCl_3$, $[2((CH_3)_2N)_2PCl]\cdot AlCl_3$ and $((CH_3)_2N)_3P\cdot((CH_3)_2N)_2PCl\cdot AlCl_3$, form easily but have been difficult to describe in conventional acid–base formalism since the analogous bis adduct containing 2 mol of $((CH_3)_2N)_3P$/mol of $AlCl_3$ could *not* be prepared. Structures of all pertinent compounds now provide an explanation. The compound $[2((CH_3)_2N)_2PCl]\cdot AlCl_3$ is shown to have the structure $[((CH_3)_2N)_3P\text{–}P(N(CH_3)_2)Cl]^+[AlCl_4]^-$, while $((CH_3)_2N)_3P\cdot((CH_3)_2N)_2PCl\cdot AlCl_3$ has the structure $[((CH_3)_2N)_3P\text{–}P(N(CH_3)_2)_2]^+[AlCl_4]^-$. These conclusions are based on conductivity data, NMR spectra for ^1H and ^{31}P nuclei, infrared spectral data, and chemical information. The compound $((CH_3)_2N)_3P\cdot AlCl_3$ which will *not* add additional $((CH_3)_2N)_3P$ is shown to be a dimer with the initial structure $[((CH_3)_2N)_3P\text{–}P(N(CH_3)_2)_2]^+[NR_2(AlCl_3)_2]^-$. The anion does not appear stable but undergoes further rearrangement. Apparent differences in chemistry are really due to the fact that the anion $[R_2NAlCl_3]^+$ picks up a second mole of $AlCl_3$ very easily. The $[GaCl_4]^-$ and $[PF_6]^-$ salts of the diphosphorus cation have been prepared, but we were not able to prepare $[((CH_3)_2N)_3P\text{–}P(N(CH_3)_2)F]^+$ in which a fluoride ion is coordinated to one phosphorus atom of the cation.

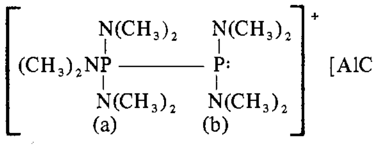
In the first paper of this series[1] interactions between (dimethylamido)chlorophosphorus(III) ligands and aluminum chloride were described. Conventional one to one addition compounds of the general formula $((CH_3)_2N)_nCl_{3-n}P\cdot AlCl_3$ were reported along with *two* unexpected two to one addition compounds of formulas $[2((CH_3)_2N)_2PCl]\cdot AlCl_3$ and $((CH_3)_2N)_3P\cdot((CH_3)_2N)_2PCl\cdot AlCl_3$. 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 $((CH_3)_2N)_3P$ and $AlCl_3$ could be prepared. *All attempts to prepare* $[2((CH_3)_3N)_3P]\cdot AlCl_3]$ *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 $[(CH_3)_3P\text{–}P(CH_3)_2]^+$ reported by Nöth[2a] and related species reported by Summers and Sisler[2b] gave a satisfactory representation of all observed properties. The compound $[2((CH_3)_2N)_2PCl]\cdot AlCl_3]$ is best described by structural formula I. The related compound $((CH_3)_2N)_3P\cdot[(CH_3)_2N)_2PCl\cdot AlCl_3$ is best described by structural formula II. The evidence to support these assertions follows.



$$\left[\underset{(a)}{(\mathrm{CH_3})_2\mathrm{N}\overset{\mathrm{N(CH_3)_2}}{\underset{\mathrm{N(CH_3)_2}}{\mathrm{P}}}}\text{———}\underset{(b)}{\overset{\mathrm{N(CH_3)_2}}{\underset{\mathrm{Cl}}{\mathrm{P}{:}}}}\right]^+ [\mathrm{AlCl_4}]^-$$

I



$$\left[\underset{(a)}{(\mathrm{CH_3})_2\mathrm{N}\overset{\mathrm{N(CH_3)_2}}{\underset{\mathrm{N(CH_3)_2}}{\mathrm{P}}}}\text{———}\underset{(b)}{\overset{\mathrm{N(CH_3)_2}}{\underset{\mathrm{N(CH_3)_2}}{\mathrm{P}{:}}}}\right]^+ [\mathrm{AlCl_4}]^-$$

II

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 $AlCl_3$ in methylene chloride has an *equivalent conductance* of $0.21 \pm 0.01\ \Omega^{-1}\ cm^2\ equiv^{-1}$. A comparable 10^{-2} M solution of $((CH_3)_2N)_2PCl$ has an equivalent conductance of less than $0.001\ \Omega^{-1}\ cm^2\ equiv^{-1}$. On the other hand, a 0.3 M solution of $[2((CH_3)_2N)_2PCl]\cdot AlCl_3$ has an equivalent conductance of $22.2 \pm 0.3\ \Omega^{-1}\ cm^2\ equiv^{-1}$. A simple ionic halide reference such as a 0.3 M solution of $[(C_6H_5)_4P]Cl$ in methylene chloride gave a value of $2.7 \pm 0.3\ \Omega^{-1}\ cm^2\ equiv^{-1}$, and a reference covalent system such as $C_6H_4Br_2$ gave a conductance of $0.0008\ \Omega^{-1}\ cm^2\ equiv^{-1}$ under comparable conditions. Clearly an ionic representation is appropriate.[3]

In the first paper of this series[1] a molecular weight value of 430 ± 60 was obtained from vapor pressure depression measurements in CH_2Cl_2, while a theoretical value of 443 was expected for $[2((CH_3)_2N)_2PCl]\cdot AlCl_3$. The data would be consistent with a mildly dissociated ionic system (Structure I) in methylene chloride.

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