steric hindrance or to the absence of hydrogen bonding (which could occur in crystals of the ammonia and primary and secondary amine complexes). The latter group of complexes would then have the more common, less symmetrical type of structure.

Carrying over this structural speculation to a discussion of the internal oxidation–reduction reactions leads to a consideration of the mechanism of amine oxidation. Such a mechanism involves an over-all two-electron oxidation coupled with a one-electron reduction. One-electron oxidation to an amine radical ion, which then undergoes disproportionation, has been postulated.[5,19] For such a disproportionation, the proximity of two one-electron oxidation products in the metal complex structure would be important and would depend on the coordination symmetry. An alternative possibility would be transfer of two electrons from an amine into the molecular orbitals the polynuclear copper(II) system. The failure of irradiation in the charge-transfer bands of the complexes to promote decomposition and the lack of antiferromagnetic interactions in the complexes would seem to make this alternative less probable.

Predissociation of the bis(ethyl- and diethylamine) complexes to 1:1 complex intermediates would presumably result in five-coordinate structures, one axial amine ligand position being vacated. Predissociation of dichlorodiamminecopper(II) to a 1:1 complex prior to its irreversible decomposition by oxidation–reduction has also been reported.[20] Complexes having such coordinatively unsaturated structures apparently are then more reactive with respect to internal oxidation–reduction.

Acknowledgments.—We wish to thank Professor Gordon Tollin for obtaining the epr spectra. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. The research was also supported in part by the National Institutes of Health, Public Health Service, through Grant GM 12642-01. The X-ray and far-infrared equipment were obtained with Institutional Grants from the National Science Foundation, for which we express our thanks.

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[19] J. T. Yoke, J. F. Weiss, and G. Tollin, *Inorg. Chem.*, **2**, 1210 (1963), and references therein.

[20] J. P. Smith and W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, **26**. 1157 (1964).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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The Reaction of Dimethylaminodifluorophosphine with Copper Chlorides[1]

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$(CH_3)_2NPF_2$ will form complexes with CuCl. The formation constants of the complexes $CuCl[(CH_3)_2NPF_2]$ and $CuCl[(CH_3)_2NPF_2]_2$ have been determined by isothermal pressure–composition phase studies. On the basis of infrared and nmr spectroscopy, it is suggested that the bonding occurs through the phosphorus atom rather than the nitrogen atom. Enhancement of the basicity of the phosphorus atom in the ligand by donation of the nitrogen electron pair to the empty phosphorus d orbitals is postulated. $CuCl_2$ will oxidize $(CH_3)_2NPF_2$ to the phosphorane, $(CH_3)_2NPF_2Cl_2$. This new phosphorane has been completely characterized by chemical analysis, molecular weight, and infrared and nmr spectroscopy.

Introduction

Recent investigations have demonstrated the coordinating ability of the ligand dimethylaminodifluorophosphine, $(CH_3)_2NPF_2$, with various electron acceptors. Ter Haar and Sr. Fleming[2] working in this laboratory noted that the ligand will displace carbon monoxide from B_4H_8CO to give $B_4H_8[(CH_3)_2NPF_2]$. A similar displacement of carbon monoxide from metal carbonyls led Schmutzler[3] to the compounds $Ni[(CH_3)_2NPF_2]_4$ and $Mo(CO)_3[(CH_3)_2NPF_2]_3$. Sr. Fleming[4] reported that either borane or boron trifluoride will add to the ligand in a 1:1 ratio. Cavell[5] also reported the addition of BF_3 to $(CH_3)_2NPF_2$. A single-crystal X-ray diffraction study of the B_4H_8 adduct by Nordman and Douglas[6] has established that bonding occurs through phosphorus rather than nitrogen. Less certain, but still rather strongly suggestive data indicate that boron trifluoride coordinates to the nitrogen and not the phosphorus in this same ligand.[4]

A preliminary investigation by Gilje[7] has shown that nickel(II) bromide forms a weak complex with the ligand. In this study, the reactions of $(CH_3)_2NPF_2$ with anhydrous copper(I) chloride and copper(II) chloride have been investigated.

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[1] Presented in part at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

[2] G. Ter Haar, Sr. M. A. Fleming, and R. W. Parry, *J. Am. Chem. Soc.*, **84**, 1767 (1962).

[3] R. Schmutzler, *Inorg. Chem.*, **3**, 415 (1964).

[4] Sr. M. A. Fleming, Ph.D. Dissertation, University of Michigan, Ann Arbor, Mich., 1963.

[5] R. Cavell, *J. Chem. Soc.*, 1992 (1964).

[6] R. M. Douglas and C. E. Nordman, personal communication, 1964.

[7] J. Gilje and R. W. Parry, unpublished data.

Results

A. The System $CuCl$–$(CH_3)_2NPF_2$.—The interaction of $(CH_3)_2NPF_2$ with anhydrous copper(I) chloride was studied in detail by isothermal measurement of the pressure of the system as a function of the composition. The relevant observations can be summarized by the equations

$$CuCl + (CH_3)_2NPF_2 \longrightarrow CuCl[(CH_3)_2NPF_2]$$

$$CuCl[(CH_3)_2NPF_2] + (CH_3)_2NPF_2 \longrightarrow CuCl[(CH_3)_2NPF_2]_2$$

The 1:1 complex has a dissociation pressure of 1.8 ± 0.5 mm at 27.0° and 2.8 ± 0.5 mm at 46.5°. The 2:1 complex has a dissociation pressure of 18.5 ± 0.5 mm at 46.5°.

Both complexes are colorless, diamagnetic, and readily soluble in nonpolar solvents such as carbon tetrachloride and benzene as well as solvents which have no labile hydrogens, such as chloroform and bromoform. The molecular weight of $CuCl[(CH_3)_2NPF_2]$ indicates that it exists as a tetramer in bromoform and may be represented by the formula $\{CuCl[(CH_3)_2NPF_2]\}_4$.

B. Reaction of $CuCl_2$ with $(CH_3)_2NPF_2$.—In contrast to copper(I) chloride, which forms stable complexes with $(CH_3)_2NPF_2$, anhydrous copper(II) chloride oxidizes the phosphine $(CH_3)_2NPF_2$ to the phosphorane $(CH_3)_2NPF_2Cl_2$. Other observers have noted that salts of copper(II) halides can oxidize phosphines.[8] However, the resulting phosphoranes have never been reported as separated and identifiable products. Complete characterization of $(CH_3)_2NPF_2Cl_2$ is presented below.

In addition to $(CH_3)_2NPF_2Cl_2$ a small amount[9] of PF_3 appeared as one of the products of the reaction. The observations can best be interpreted in terms of two competing processes, both of which presumably proceed through a coordination compound intermediate. The major reaction, which involves the oxidation of the phosphine, is

$$2CuCl_2 + (CH_3)_2NPF_2 \longrightarrow [\text{complex}] \longrightarrow (CH_3)_2NPF_2Cl_2 + 2CuCl$$

If an excess of $(CH_3)_2NPF_2$ is present, the CuCl formed combines with the excess ligand to give $\{CuCl[(CH_3)_2NPF_2]\}_4$. The stoichiometry is represented by the equation

$$4CuCl_2 + 6(CH_3)_2NPF_2 \longrightarrow 2(CH_3)_2NPF_2Cl_2 + \{CuCl[(CH_3)_2NPF_2]\}_4$$

The competing and apparently slower process involves group exchange on the coordinated ligand

$$CuCl_2 + 2x(CH_3)_2NPF_2 \longrightarrow [\text{complex}] \longrightarrow CuCl_2\{[(CH_3)_2N]_2PF\}_x + xPF_3$$

Subsequent oxidation of $[(CH_3)_2N]_2PF$ or its stabilization through coordination to CuCl would then be anticipated. In support of this latter suggestion, it was noted that the X-ray powder pattern of the diamagnetic solid remaining in the reaction tube exhibits intense lines attributable to CuCl, as well as several lines of much lower intensity. The less intense lines may arise from $CuCl\{[(CH_3)_2N]_2PF\}_x$.

C. Characterization of $(CH_3)_2NPF_2Cl_2$.—$(CH_3)_2NPF_2Cl_2$ is unstable at 25°; therefore, characterization must be carried out as soon as possible after formation. The proton nmr spectrum, for example, will exhibit changes within 30 min at 25°.

Vapor density studies at 85° gave molecular weights of 191, 196, and 198. The molecular weight determinations always yielded higher values than the theoretical value of 184. The higher values are attributed to the formation of a nonvolatile solid during the measurement.

Vapor pressure data for $(CH_3)_2NPF_2Cl_2$ follow the equation

$$\log P_{\text{mm}} = \frac{-2022}{T} + 77.2$$

The Trouton constant is 22.1 cal mole^{-1} deg^{-1}; the extrapolated normal boiling point is 144°. Vapor pressure data can be summarized in the following sequence [temperature (°K), observed vapor pressure (mm) (calculated vapor pressure)]: 299, 8.6 (9.1); 308, 13.0 (14.4); 316, 20.2 (21.2); 320, 28.0 (25.5); 328, 34.0 (36.1); 336, 51.2 (50.8); 345, 69.1 (71.7); 350, 98.0 (88.0); 360, 115.1 (127.2). Some decomposition was observed at higher temperatures where agreement between calculated and observed values is poor.

The formula $(CH_3)_2NPF_2Cl_2$ is supported by the proton and fluorine nmr spectra. The proton spectrum shows a 1:1 doublet (δ −2.83 ppm), due to P–N–C–H coupling ($J_{\text{PNCH}} = 13.2$ cps). Each member of the doublet is split into a 1:2:1 triplet by F–P–N–C–H coupling ($J_{\text{FPNCH}} = 2.7$ cps). The P–H coupling constant of 13.2 cps is only slightly larger than the value of 9.0 cps reported for $(CH_3)_2NPF_2$.[4,10] The F–H coupling constant of 2.7 cps is very slightly smaller than the value of 3.6 cps reported for $(CH_3)_2NPF_2$.[4,10]

The fluorine resonance signal is also split into a 1:1 doublet (δ −54.3 ppm from CF_3Cl) by P–F coupling. The J_{PF} value of 949 ± 8 cps is between the value of 1194 cps reported for $(CH_3)_2NPF_2$[4,10] and the value of 836 cps reported for $(CH_3)_2NPF_4$.[11]

Muetterties and co-workers[12,13] have established that most five-coordinate phosphorus(V) derivatives have a trigonal-bipyramidal coordination about the phosphorus atom, with the most electronegative groups at the axial sites of the trigonal bipyramid. On the basis of this work, the structure for $(CH_3)_2NPF_2Cl_2$ may be designated as a trigonal bipyramid in which the two fluorine atoms are located at the axial positions. To some extent this view is supported by the lack of broad-

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(8) G. Booth, *Advan. Inorg. Chem. Radiochem.*, **6**, 47 (1964), and references therein.

(9) Usually less than a 10% yield based on amount of $(CH_3)_2NPF_2$ which reacts.

(10) R. Schmutzler and G. S. Reddy, *Z. Naturforsch.*, **20b**, 104 (1965).

(11) D. H. Brown, G. W. Fraser, and D. W. A. Sharp, *J. Chem. Soc., Sect. A*, 171 (1966).

(12) E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, **3**, 1298 (1964).

(13) E. L. Muetterties, W. Mahler, and R. Schmutzler, *ibid.*, **2**, 613 (1963).

ening in the ^{19}F nmr spectra at −20°. In addition, the value of the chemical shift of the fluorines on $(CH_3)_2NPF_2Cl_2$ is lower than any chemical shift reported for fluorines in the equitorial position, but is similar to the chemical shift for the axial fluorines of Cl_2PF_3 (−67 ppm from CF_3Cl) and n-$C_3F_7PCl_2F_2$ (−40.2 ppm from CF_3Cl).[14]

Under higher resolution each member of the fluorine doublet is further split into a 1:6:15:20:15:6:1 septet by coupling with six equivalent protons. The P–H coupling constant obtained from the fluorine resonance signal is identical within experimental error to that obtained from the proton spectrum, 2.7 cps.

Dimethylaminodifluorodichlorophosphorane is a colorless liquid at room temperature. It is reactive with water, moist air, and amines. As mentioned previously, the liquid slowly undergoes transformation to solid. This behavior appears typical of the mixed fluorohalides of pentavalent phosphorus. Kennedy and Payne[15] noted that PF_3Cl_2 turned to a solid and assigned the formula $[PCl_4^+][PF_6^-]$ to the solid phase. The conversion of the covalent PCl_4F to the ionic $[PCl_4^+]F^-$ isomer has been investigated in detail by Kolditz.[16] Nixon[17,18] reported that trichloromethyldichlorodifluorophosphorane, $CCl_3PF_2Cl_2$, in contrast to other mixed fluorohalides of pentavalent phosphorus, forms no ionic species. Thus the trichloromethyl group attached to the PF_2Cl_2 moiety hinders conversion to an ionic solid, but the sterically comparable dimethylamino group seems to have no such effect.

The infrared spectrum of $(CH_3)_2NPF_2Cl_2$ vapor shows absorption at 2940 (m), 1510, 1495, 1485, 1465 (m), 1370 (vs), 1315, 1190 (m), 1015 (s), 885 (vs), and 702 (w) cm^{-1}. It was noted that the infrared spectrum exhibits changes after 2 hr owing to decomposition.

Anal. Calcd for $(CH_3)_2NPF_2Cl_2$: C, 13.05; H, 3.29; N, 7.61; Cl, 38.55. Found: C, 13.13; H, 3.39; N, 7.57; Cl, 37.61.

Experimental Section

Because all of the compounds employed in the reactions are sensitive to traces of moisture or oxygen, the reactions were carried out using standard high-vacuum techniques. Solid materials were handled in an atmosphere of dry nitrogen.

Materials and Analyses.—Dimethylaminodifluorophosphine was prepared by the method of Schmutzler[3] using antimony trifluoride (Alfa Inorganics, Inc.) and dimethylaminodichlorophosphine.[19] The identity of $(CH_3)_2NPF_2$ was established by comparison of its infrared, proton nmr, and fluorine nmr spectra with the previously reported spectra[4,10]; by a vapor density molecular weight of 113; and by a vapor pressure of 93.6 mm at 0° (lit.[4] pressure 93.4 mm). Anhydrous copper(I) chloride was prepared from reagent grade hydrated copper(II) chloride (Baker) using the sulfite reduction technique.[20] Anhydrous copper(II) chloride was prepared from hydrated copper(II) by dehydration with thionyl chloride (Eastman).[21] The elemental analyses were carried out by Sprang Microanalytical Laboratories, Ann Arbor, Mich.

Phase Diagram for CuCl.—Because of the high dissociation pressures of the $CuCl[(CH_3)_2NPF_2]$ and $CuCl[(CH_3)_2NPF_2]_2$ complexes, it was necessary to construct an isothermal pressure–composition phase diagram to examine in detail the interaction of the anhydrous copper(I) chloride with $(CH_3)_2NPF_2$. These were prepared using a modification of the method described by Yoke.[22]

A known amount of pure $(CH_3)_2NPF_2$ was condensed onto a weighed sample of the anhydrous copper(I) chloride in a tube connected to a mercury manometer attached to a high-vacuum system. The tube, still connected to the manometer, was sealed and removed from the vacuum system. The system was maintained at a constant temperature for a period of time ranging from 3 weeks to 4 months, after which time the pressure of the system was measured. Each point on the phase diagram was therefore obtained independently.

After equilibrium was obtained at one temperature and the pressure measured, the equilibrium was disturbed by raising the system to a new, higher temperature for 1 day. At the end of the day, the temperature was lowered to its original value, and the system allowed to reequilibrate for 2 or 3 weeks. At the end of this time, the pressure was again measured. When the original pressure was identical with the final pressure, it was certain that equilibrium had been obtained. An alternate method involved cooling the system.

The isothermal phase diagram for the system CuCl–$(CH_3)_2NPF_2$ at 46.5° is shown in Figure 1. The horizontal portion of the phase diagram from mole ratio 0.0 to mole ratio 1.0 followed by the sharp break at mole ratio 1.0 indicates the formation of a 1:1 complex. On the other hand, the horizontal portion of the phase diagram between mole ratios of 1 and 2 indicates either the formation of a saturated solution of the 1:1 complex in excess $(CH_3)_2NPF_2$, or the formation of a complex containing 2 moles of ligand to 1 mole of copper(I) chloride. Verification of formation of a 2:1 complex was obtained from the X-ray powder patterns of copper(I) chloride,[23] the 1:1 complex, and a mixture of 2.0 moles of $(CH_3)_2NPF_2$ to 1.0 mole of copper (I) chloride. As shown in Table I, the pattern of the 2:1 mixture exhibits lines which are attributable to neither copper(I) chloride nor the 1:1 complex.

The curvature shown in the phase diagram in the region between mole ratio 2 and 3 is attributed to a decrease in the vapor pressure of the ligand due to solubility of the complexes in excess $(CH_3)_2NPF_2$.

Other Preparations of $CuCl[(CH_3)_2NPF_2]$.—Although the phase diagram indicates the existence of a 1:1 complex between $(CH_3)_2NPF_2$ and CuCl, the complex was also prepared by three related methods which verify its existence.

The first method takes advantage of the fact that the dissociation pressure of the 1:1 complex is less than the dissociation pressure of the 2:1 complex. In a typical reaction 0.750 g (7.50 mmoles) of white, anhydrous copper(I) chloride was transferred in a dry inert atmosphere to a tared 55-cc reaction tube which was equipped with a stopcock, a standard taper joint, and a magnetic stirring bar. The tube was evacuated and about 3 g of pure $(CH_3)_2NPF_2$ was condensed in the tube at −196°. The mixture was warmed to 65° on a water bath and stirred until all of the copper(I) chloride dissolved. The mixture was then cooled to 0°, and the pressure above the mixture reduced to 10^{-4} mm by opening the reaction tube to the vacuum pumping system. After 3 days, 0.8536 g (7.55 mmoles) of ligand remained on the copper(I) chloride, indicating the formation of a 1:1 complex. If the mixture was allowed to warm to room temperature, only

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[14] (a) R. Schmutzler, *Advan. Fluorine Chem.*, **5**, 252 (1965); (b) R. Schmutzler, "Fluorophosphoranes," International Review on Halogen Chemistry, Academic Press Inc., New York, N. Y., in press, and references therein. We are indebted to R. Schmutzler for a prepublication copy of this review.

[15] T. Kennedy and D. S. Payne, *J. Chem. Soc.*, 1228 (1959).

[16] L. Kolditz, *Z. Anorg. Allgem. Chem.*, **293**, 147 (1957).

[17] J. F. Nixon, *J. Inorg. Nucl. Chem.*, **27**, 1281 (1965).

[18] J. F. Nixon, *Chem. Ind.* (London), 1555 (1963).

[19] A. B. Burg and P. J. Slota, *J. Am. Chem. Soc.*, **80**, 1107 (1958).

[20] R. N. Keller and H. D. Wycoff, *Inorg. Syn.*, **2**, 1 (1946).

[21] A. R. Pray, *ibid.*, **5**, 153 (1957).

[22] J. T. Yoke, Ph.D. Dissertation, University of Michigan, Ann Arbor, Mich., 1954.

[23] R. W. G. Wyckoff and E. Posnjah, *J. Am. Chem. Soc.*, **44**, 30 (1922).

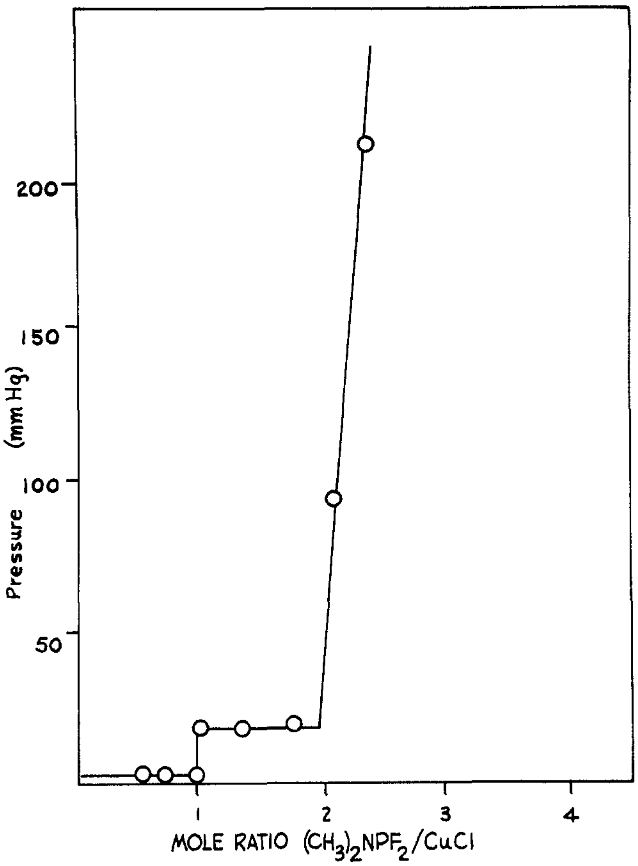

Figure 1.—Isothermal pressure–composition phase diagram for $CuCl_2$–$(CH_3)_2NPF_2$ at 46.5°.

TABLE I

INTERPLANAR SPACING AND RELATIVE INTENSITY DATA

$\{CuCl[(CH_3)_2NPF_2]\}_4$			$CuCl[(CH_3)_2NPF_2]_2$		
2θ	d, A	Intens	2θ	d, Å	Intens
7.3	12.1	vs	11.55	8.4	vs
8.0	11.0	vs	15.50	5.71	s
11.0	8.0	w	12.75	6.94	m
12.5	7.1	w	18.20	4.87	w
14.2	6.2	w	22.05	4.03	w
21.8	4.07	w	24.55	3.62	w
26.5	3.36	w	30.30	2.95	w
32.5	2.75	w	32.00	2.79	w

pure CuCl and $(CH_3)_2NPF_2$ were recovered. Difficulty was encountered occasionally in this procedure. The 2:1 complex is inevitably formed and with larger amounts of reactants the time required to remove the excess ligand and form only the 1:1 complex is prohibitive.

Another procedure simply involved mixing $(CH_3)_2NPF_2$ and CuCl in a mole ratio of 1:1. The mixture was then alternately heated to 65° and cooled to 0° several times until the pressure above the system was about 3 mm at 25°.

In a third procedure, small, known increments of $(CH_3)_2NPF_2$ were condensed *in vacuo* onto a known weight of copper(I) chloride suspended in benzene. At a ratio of 1.03 moles of $(CH_3)_2NPF_2$ to 1.00 mole of copper(I) chloride, the copper(I) chloride dissolved completely, indicating formation of a soluble 1:1 complex.

Reaction of $CuCl_2$ with $(CH_3)_2NPF_2$.—In a typical reaction 4.54 mmoles of brown, anhydrous $CuCl_2$ was transferred in a dry, inert atmosphere to a 55-cc reaction tube which was equipped with a stopcock, a standard taper joint, and a magnetic stirrer. The tube was evacuated and a 22.99-mmole sample of pure $(CH_3)_2NPF_2$ was condensed in the tube at −196°. After warming to 15°, the contents of the tube was stirred for 10 min. The brown copper(II) chloride first turned black, possibly indicating complex formation, and then dissolved with effervescence to form a pale yellow solution. The tube was quickly opened to the vacuum pumping system through two −196° traps to recover the volatile components. After pumping on the system for 3 days at 25°, the temperature of the tube was raised to 60°.

The products collected in the −196° traps were passed through traps at −63, −119, and −196°. A 0.16-mmole sample of PF_3, identified by its infrared spectrum and a vapor density molecular weight of 88, was trapped at −196°. A 20.37-mmole sample of unreacted $(CH_3)_2NPF_2$ was recovered from the −119° trap. The −63° trap contained 2.06 mmoles of $(CH_3)_2NPF_2Cl_2$. The $(CH_3)_2NPF_2Cl_2$ was fully characterized as described previously. The experimental stoichiometry of the reaction is

$$2.00CuCl_2 + 1.15(CH_3)_2NPF_2 \longrightarrow 0.07PF_3 + 0.91(CH_3)_2NPF_2Cl_2 + \text{solid}$$

The solid was identified by its X-ray powder pattern. This pattern exhibited intense lines which were identical with those obtained from an authentic sample of CuCl. In addition to these lines, the pattern also exhibited several lines of much lower intensity. These less intense lines could not be attributed to either $CuCl[(CH_3)_2NPF_2]$ or $CuCl[(CH_3)_2NPF_2]_2$. Because the solid was diamagnetic, the possibility of any Cu(II) complexes was reduced. The production of PF_3 suggests the presence of $CuCl\{[(CH_3)_2N]_2PF\}_x$ in the reaction mixture.

In other runs, it was found that the amount of PF_3 produced can be increased by lengthening the time the reactants remain in contact with each other, or by raising the temperature of the reaction.

Reaction of $(CH_3)_2NPF_2$ with Cl_2 to Produce $(CH_3)_2NPF_2Cl_2$.—Further evidence of the identity of $(CH_3)_2NPF_2Cl_2$ was obtained by the oxidation of $(CH_3)_2NPF_2$ directly by anhydrous chlorine. The product thus obtained was identical in every respect with the product obtained from the reaction of $CuCl_2$ and $(CH_3)_2NPF_2$.

In a typical reaction 0.156 g (2.06 mmoles) of chlorine was condensed at −196° *in vacuo* into a 62-cc reaction tube equipped with a stopcock and a standard taper joint. While the tube was maintained at −196°, 3.21 mmoles of $(CH_3)_2NPF_2$ was distilled *in vacuo* onto the solid chlorine. The reaction products were passed through traps at −63 and −196°. A 1.14-mmole sample of unreacted $(CH_3)_2NPF_2$ was recovered from the −196° trap, indicating a 1:1 reaction between the phosphine and chlorine. The −63° trap contained a clear liquid whose infrared and ^1H and ^{19}F nmr spectra were identical with that of $(CH_3)_2NPF_2Cl_2$ produced by the reaction of $(CH_3)_2NPF_2$ and $CuCl_2$.

Infrared Spectra.—The infrared spectra were obtained on a Perkin-Elmer Model 337 grating spectrometer. For volatile materials a gas cell with 7.5-cm path length and KBr windows was used. Solid materials were examined as mulls prepared in an atmosphere of dry nitrogen using a drybox.

Nuclear Magnetic Resonance Spectra.—Proton nmr spectra were observed on a Varian Model A-60 nuclear magnetic resonance spectrometer operating at the ambient temperature of the instrument. Fluorine nmr spectra were observed on a Varian Model HR-100 nuclear magnetic resonance spectrometer operating at 94.1 Mc at the temperature previously mentioned. For the proton spectra tetramethylsilane was used as an internal standard. For fluorine magnetic resonances trichlorofluoromethane was used as a reference by the tube-interchange technique. Whenever possible, the samples were run as neat liquids. For solids appropriate solvents were used, as noted.

X-Ray Powder Photographs.—Standard techniques previously described[24] were used in this study. Samples were loaded into glass capillaries of 0.03-mm inner diameter and a wall thickness of 0.01 mm. A 11.4-cm Debye–Scherrer camera was used both for identification purposes and for determination of interplanar spacings. A General Electric XRD-1 X-ray unit emit-

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(24) C. W. Bunn, "Chemical Crystallography," Cornell University Press, Ithaca, N. Y., 1948, Chapter 5.

ting nickel-filtered copper Kα radiation was used. Kodak No-Screen Medical X-ray film was placed in the camera.

Discussion

Copper(I) Chloride.—An early X-ray analysis by Wells[25,26] of an arsine complex of copper(I) iodide, $\{CuI[As(C_2H_5)_3]\}_4$, can be used as the basis for suggesting the structure of $\{CuCl[(CH_3)_2NPF_2]\}_4$. The four copper atoms in the postulated structure lie at the corner of a regular tetrahedron; the four chloride ions lie above the center of each tetrahedral face, while the phosphine is coordinated directly to the copper on a line extending outward on each threefold rotational axis of the tetrahedron. This structure is best understood if it is realized that $(CH_3)_2NPF_2$ bonds through the phosphorus atom and is therefore analogous to alkylphosphines or arsines in its bonding properties.

It is worth mentioning at this point that efforts to isolate a complex between copper(I) chloride and PF_3 were reported as unsuccessful,[27] which illustrates the enhancement of the donating ability of the PF_2 moiety by the $(CH_3)_2N$ group. This enhancement is also useful in explaining phosphorus acting as the bonding site. The enhancement may be made comprehensible if it is realized that the lone electron pair of nitrogen may be shared to some extent by the phosphorus, which has available 3d orbitals. An electronic interaction of this type would enhance the ability of phosphorus to participate in σ bonding with electron acceptors, while simultaneously lowering the donating power of the nitrogen electrons. Therefore, $(CH_3)_2NPF_2$ is expected to be a better donor than PF_3; metals able to complex PF_3 should also complex $(CH_3)_2NPF_2$.

The pertinent experimental data supporting the structural proposal for $\{CuCl[(CH_3)_2NPF_2]\}_4$ are discussed below.

(1) **The Infrared Spectrum of $\{CuCl[(CH_3)_2NPF_2]\}_4$.**—The infrared spectra of the complex mulled in halocarbon and Nujol have been obtained. As can be seen from the data presented in Table II, the spectrum of the complex is very similar to that of the uncomplexed ligand, as expected.[28] In particular, the absorption in the region 2760–2820 cm^{-1} is virtually identical in the complexed and uncomplexed ligand as shown in Figure 2. This fact is significant since in an empirical study of many different nitrogen complexes containing the $>\overline{N}-CH_3$ group, Sheppard and coworkers[29] correlated the absorption in this region with a carbon–hydrogen stretch, modified by the presence of an unshared electron pair on the nitrogen. In Sheppard's study this stretching frequency disappeared upon salt formation or upon coordination of the nitrogen. This same generalization has been confirmed in this laboratory. Because the 2820-cm^{-1} absorption remains in the copper(I) chloride complex, an uncoordinated nitrogen appears to remain and coordination through phosphorus is suggested.

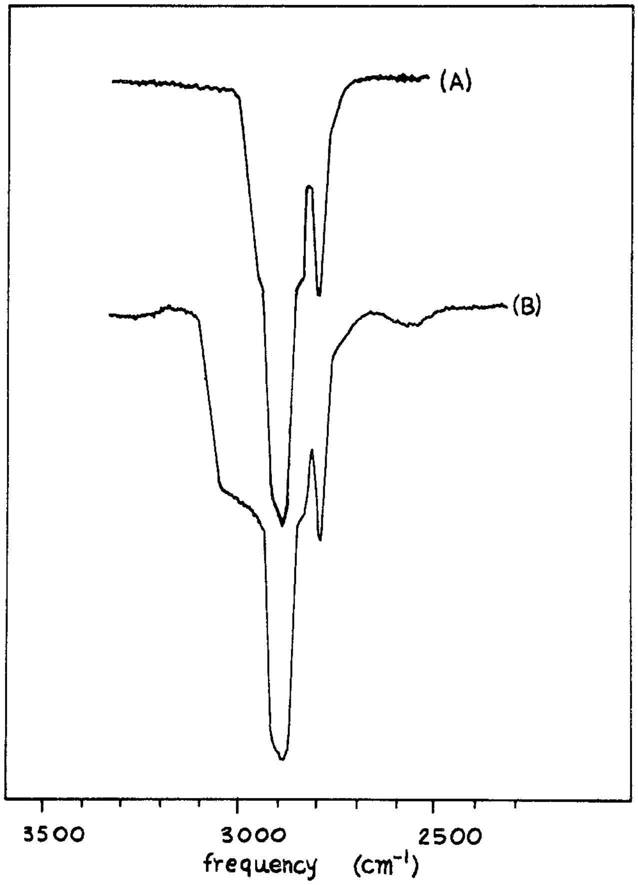

Figure 2.—Infrared spectrum of uncomplexed $(CH_3)_2NPF_2$ (A) and $[CuCl((CH_3)_2NPF_2)]_4$ (B).

Table II

Comparison of the Infrared Spectra

$(CH_3)_2NPF_2(g)$[4]	$\{CuCl[(CH_3)_2NPF_2]\}_4(s)$
	3050 sh[a]
2925 m	2925 m
2865 sh	2865 sh
2820 w	2820 w
1507–1432 w	1510–1430 m
1307 m	1320 m
1195 m	1190 m
1073 w	1070 w
989 s	995 s
814 s	815 s
770 s	760 s
704 m	712 m

[a] Impurity in Fluorolube.

(2) **The Nmr Spectra of $\{CuCl[(CH_3)_2NPF_2]\}_4$.**—The proton nmr spectrum of the complex dissolved in benzene consists of a 1:1 doublet (δ 2.83 ppm) due to H–C–N–P coupling. Each member of the doublet is further split into a 1:2:1 triplet by coupling of the hydrogen with two equivalent fluorines. The HCNP coupling constant of 11.8 cps is slightly higher than the value of 9.0 cps reported for the uncomplexed ligand.[4,10] The HCNPF coupling constant is identical within experimental error with that of the uncomplexed ligand, 3.6 cps.[4,10]

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The fluorine nmr spectrum also consists of a 1:1 doublet (δ +53 ppm from CCl_3F) caused by coupling of the fluorine with phosphorus. The P–F coupling constant is identical within experimental error to that of the uncomplexed ligand, 1194 cps.

Although $\{CuCl[(CH_3)_2NPF_2]\}_4$ is quite soluble in nonpolar organic solvents, several attempts to obtain the phosphorus nmr spectrum were unsuccessful. The difficulty can be traced to two obstacles. First, owing to the low magnetogyric ratio of phosphorus, the signal is about 10 times less intense than either hydrogen or fluorine. Second, because phosphorus is directly attached to the copper atom, the signal is expected to be broadened as a result of the quadrupole relaxation induced by copper. The signal is so broad that it cannot be located.

Copper(II) Chloride.—The oxidation–reduction reaction between $(CH_3)_2NPF_2$ and copper(II) chloride is not surprising. All phosphines[8] and some amines[30] also undergo oxidation by copper(II) halides. In the reaction of $(CH_3)_2NPF_2$ with $CuCl_2$ the formation of a new compound, $(CH_3)_2NPF_2Cl_2$, clearly indicates that any scheme used to rationalize the oxidation–reduction reaction must involve both an electron and an atom transfer. The mechanism of this reaction is not yet understood.

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The Effect of Hydroxylic Solvents on the Kinetic Behavior of Gold(III) Complexes

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The role of seven hydroxylic solvents ($C_6H_5CH_2OH$, CH_3OH, C_2H_5OH, C_3H_7OH, i-C_3H_7OH, $CH_3OCH_2CH_2OH$, $C_2H_5OCH_2CH_2OH$) on the rates of the reactions in which heterocyclic amines (pyridine, 3-methylpyridine, 3,4-dimethylpyridine) are either the leaving or entering group in processes of the type $AuCl_3(am) + Y^-$ and $AuCl_4^- + am$ have been studied. The results indicate that the sequence of solvent effect upon the second-order rate constants is unaffected by the nature of the amine but is quantitatively reversed on going from the reactions of $AuCl_4^-$ with amines to those of the neutral $AuCl_3(am)$ with chloride and, to a smaller extent, bromide anion. This is discussed in terms of relative solvation of the charged species in the ground and transition states.

Introduction

The displacement of the coordinated amine from complexes of the type $AuCl_3(am)$ by various nucleophiles was studied[1,2] in methanol at 25°. Linear relationships between the free energy of activation and the basicity of the leaving amine were found when the entering nucleophiles are essentially σ bonded (*e.g.*, Cl^- and Br^-), whereas biphilic reagents (NO_2^- and N_3^-) cause a more complicated behavior. The work was extended[3] to a study of the reverse reactions, namely, the displacement of chloride from tetrachlorogold(III) anion by various pyridine derivatives under the same experimental conditions. The equilibrium constants for the process

$$AuCl_4^- + am \rightleftharpoons AuCl_3(am) + Cl^- \qquad (1)$$

were calculated from the ratio of the second-order rate constants of the reverse and forward reactions. The results were discussed in terms of the influence of the basicity and, in some cases, of the steric hindrance of the amines upon both the kinetic and equilibrium constants.

Having established the factors governing the effect of the entering and leaving groups upon this type of reactions, it appeared necessary to investigate, in detail, the role played by the solvent. In this paper we report and discuss the kinetics and equilibria of process 1 (in the cases where am = pyridine, 3-methylpyridine, and 3,4-dimethylpyridine) in a series of hydroxylic solvents. In addition, we report the effect of changing the solvent upon the reaction

$$AuCl_3(am) + Br^- \longrightarrow AuCl_3Br^- + am$$

Results and Discussion

In the case of the reactions involving the entry of chloride, the ultraviolet spectra at the beginning and at the end of the reactions correspond exactly to those of authentic samples of $AuCl_3(am)$ and $AuCl_4^-$ (and *vice versa* for the reverse processes) in each of the examined solvents. During the reactions isosbestic

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