from this solution left a chloride-free material which exhibited an average molecular weight of 950 (Rast method).

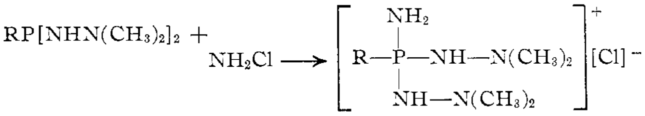
The infrared spectrum of this material contains the broad absorption band characteristic of the phosphonitrilic linkage in the region 1000–1420 cm.$^{-1}$. Thus it appears that this material contains phosphonitrilic species and is probably a mixture of a variety of such species. Thin layer chromatography on silica, as well as fractional crystallization from chloroform, failed to effect a separation of the phosphonitrilic components of the mixture.

Treatment of this material with water transforms it to a tan powder, which when dry exhibits nonwetting properties in that it forms a dry film on a water surface and is wetted only with difficulty and has an average molecular weight of 900 (Rast method) and an infrared spectrum very similar to that of the parent material. Again, thin layer chromatography on silica and fractional crystallization from chloroform or benzene failed to effect a separation of the components present.

Pyrolysis of bis(2,2-dimethylhydrazino)aminomethylphosphonium chloride under identical conditions produced a brown glassy solid residue which was essentially insoluble in chloroform or benzene. The infrared spectrum of this material shows a strong broad absorption in the 1000–1420 cm.$^{-1}$ region. This indicates that the presence of a major amount of a mixture of phosphonitrilic materials is highly probable.

Discussion

The results of the experiments described above clearly indicates that the chloramination of the bis(2,2-dimethylhydrazino)phosphines studied may be represented by the equation



$$RP[NHN(CH_3)_2]_2 + NH_2Cl \longrightarrow \left[R-\overset{NH_2}{\underset{NH-N(CH_3)_2}{P}}-NH-N(CH_3)_2 \right]^+ [Cl]^-$$

($R = CH_3$ or C_6H_5)

It is thus established that even when two hydrazino groups are attached to the phosphorus atom all of the hydrazino nitrogen atoms are inert to chloramination, even when the phosphorus atom is made unavailable for reaction with chloramine by formation of the bis(hydrazino)phosphine oxide. In the reaction of bis(2,2-dimethylhydrazino)phenylphosphine oxide with the ammonia–chloramine mixture the infrared spectrum of the resultant products plus the fact of the recovery of the starting material indicate that the only change which occurs is the formation of ammonium chloride (and presumably nitrogen) from the reaction of chloramine and ammonia. It is probable that this reaction may have been catalyzed by the presence of the phosphine oxide.

The pyrolysis of bis(2,2-dimethylhydrazino)aminophenylphosphonium chloride obtained from the chloramination of the corresponding bis(hydrazino)phosphine yields ammonia, 1,1-dimethylhydrazine, a small amount of nitrogen gas, and a very small amount of an unidentified basic nitrogen compound which, however, is not methylamine, dimethylamine, or hydrazine. The glassy residue is shown by its infrared spectrum and composition to probably contain a major amount of a mixture of phosphonitrilic derivatives with an average molecular weight of 950 (Rast method) plus some ammonium chloride. A similar material (most likely polymeric) was obtained from the pyrolysis of bis(2,2-dimethylhydrazino)aminomethylphosphonium chloride.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Difluoroaminooxyperfluoromethane, CF_3ONF_2

BY JEAN'NE M. SHREEVE, LEONARD CLINTON DUNCAN,
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The colorless, gaseous compound, CF_3ONF_2, has been prepared by the reaction of CF_3OF with N_2F_4 and by the basic hydrolysis of $CF_3OSF_4NF_2$.

A mixture of CF_3OF and N_2F_4 at initial pressures of 251 and 130 mm., respectively, in a 1.2-l. nickel vessel was held at room temperature, about 23°, for 21 hr. Products which were identified through infrared spectra after separation by fractional codistillation included CF_4, NF_3, COF_2, and SiF_4 (which must have formed in the glass vacuum system for handling the material), as well as unreacted CF_3OF and N_2F_4. Two other compounds found were CF_3ONF_2 and a small amount of an unidentified product with a boiling point near room temperature.

When 223 mm. of CF_3OF (contaminated with COF_2 and CF_4) and 209 mm. (36 mmoles) of N_2F_4 were mixed in a 3.2-l. Pyrex bulb and irradiated through a quartz finger for 3 hr., about 13 mmoles of CF_3ONF_2 was formed. A Hanau high-pressure ultraviolet lamp, Type 81, was used. Other components of the product mixture included NF_3, $(NO)_2SiF_6$, and unreacted starting materials. Although Pyrex glass vessels may be used for the preparation, it is more convenient to use metal vessels without ultraviolet irradiation to preclude the formation of large quantities of $(NO)_2SiF_6$.

Partial conversion to CF_3ONF_2 occurred, as was indicated by an infrared spectrum of the residual gases, when a sample of gaseous $CF_3OSF_4NF_2$[1] was held for 3 days at room temperature in a Pyrex glass flask which contained an excess of 1 *M* aqueous sodium hydroxide solution. When the mixture of gases was then held in contact with 2 *M* NaOH for 2 hr. at about 67°, no $CF_3OSF_4NF_2$ remained, and the gas, after drying, was identified as substantially pure CF_3ONF_2 in a yield greater than 90%.

Difluoroaminooxyperfluoromethane was shown to have an experimentally determined molecular weight

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[1] L. C. Duncan and G. H. Cady, *Inorg. Chem.*, **3**, 1045 (1964).

of 137.0 by vapor density (137.01 theoretical for CF_3ONF_2). *Anal.* Calcd. for CF_3ONF_2: F, 69.3; N, 10.2. Found: F, 71.7; N, 10.4. Vapor pressure measurements indicate a molar heat of vaporization of 4.4 kcal. and an extrapolated boiling point of 213.4°K. Experimental vapor pressure data are as follows (T (°K.), P (mm.)): 167.7, 45.0; 179.2, 103.0; 183.2, 131.8; 188.1, 187.6; 196.2, 297.2; 206.2, 523.; 210.2, 640. Between 167.7 and 210.2°K., the equation $\log P_{mm} = 7.375 - 968.6T^{-1}$ may be used to calculate vapor pressures. The Trouton constant is 20.8.

A typical nuclear magnetic resonance spectrum is obtained with a broad triplet attributed to NF_2 ($\delta_{CFCl} = -124$ p.p.m., $J_{N-F} = 117$ c.p.s.) and a triplet to CF_3 ($\delta_{CFCl_3} = 63.0$ p.p.m., $J_{NF-CF} = 3.37$ c.p.s.). The relative peak areas are 2.0:3.0 (N–F:C–F). Positive ions observed in the mass spectrum, which was obtained with an ionizing voltage of 70 volts, listed in order of decreasing relative abundance include: CF_3^+, NF_2^+, NO^+, FCO^+, NF^+, F_2CO^+, CO^+ (or CO^+ and N_2^+), CF^+, CF_2^+. $NF_2OCF_2^+$, $NOCF_3^+$, NFO^+, and others were present in very low abundance.

The infrared spectrum obtained at 10 mm. pressure in a 5-cm. cell with sodium chloride windows consists of bands at 1302 (vs), 1240 (vs), 1218 (vs), 1026 (m), 940 (m), 890–910 (m), 869 (vs), and 715 (center of triplet) (m) cm.$^{-1}$.

The compound is stable in Pyrex glass either neat or in the presence of $CFCl_3$ at room temperature for several months. No decomposition is observed when it is held at 95° for 12 hr. However, decomposition was noted in Pyrex at 135–140° to give CF_4, NO_2, and SiF_4.

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Temperature Dependence of the Magnetic Susceptibility of Di-μ-(diphenylphosphido)bis(dicarbonylnickel)

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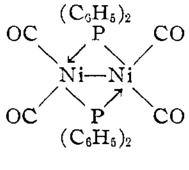
Hayter[1] has recently characterized a binuclear phosphorus-bridged complex of nickel(I) which he formulates with a metal–metal bond as



The infrared spectrum is consistent with either tetrahedral or *cis* planar geometry about the nickel atom. Room-temperature magnetic susceptibility measurements[1] gave for the corrected molar susceptibility $\chi'_M = +427 \times 10^{-6}$ c.g.s./mole. This small paramagnetism could be a temperature-independent susceptibility due to the magnetic field mixing a high-lying excited state into the ground state. On the other hand, the paramagnetism could result from the Ni–Ni bond being very weak, so that there is a thermally accessible triplet state which is appreciably occupied at room temperature. If this is so the susceptibility of $[Ni\{P(C_6H_5)_2\}(CO)_2]_2$ will exhibit a temperature dependence like that of copper acetate.[2] Finally, it may be that the paramagnetism is a consequence of the presence of a small amount of impurity with unpaired spins. If this is the case the susceptibility should follow a Curie or Curie–Weiss law.

In order to distinguish between the above three possibilities we have measured the magnetic susceptibility of $[Ni\{P(C_6H_5)_2\}(CO)_2]_2$ as a function of temperature between 298 and 120°K. The results are reported in this note.

Experimental

A sample of $[Ni\{P(C_6H_5)_2\}(CO)_2]_2$, sealed under nitrogen in a glass ampoule, was sent to us by Dr. Hayter. The sample was transferred (drybox) to a Teflon capsule which was then sealed with an air-tight closure. The susceptibility measurements were made in the standard way on a pendulum magnetometer[3] using a field of 14,200 oersteds.

Results and Discussion

The corrected[4] molar susceptibilities at twelve temperatures are given in Table I. It is clear that over the range studied the susceptibility is independent of temperature. The mean of the results in the table is $\chi'_M = 274 \pm 11 \times 10^{-6}$ c.g.s./mole. This is 35% less than the value reported for the room-temperature susceptibility. Hayter[1] has indicated that the sample used for the room-temperature measurement may have contained small amounts of Ni(II) due to surface oxidation of the crystals. This may explain the discrepancy. At any rate, it is evident from the tempera-

TABLE I

MAGNETIC SUSCEPTIBILITY OF $[Ni\{P(C_6H_5)_2\}(CO)_2]_2$

T, °K.	$10^6\chi'_M$, c.g.s./mole	T, °K.	$10^6\chi'_M$, c.g.s./mole
297	275	200	300
280	243	180	275
270	275	160	262
260	269	140	256
240	281	130	281
220	294	120	275

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[1] R. G. Hayter, *Inorg. Chem.*, **3**, 711 (1964).

[2] See, for example, B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 3837 (1956).

[3] R. M. Bozorth, H. J. Williams, and D. E. Walsh, *Phys. Rev.*, **103**, 572 (1956).

[4] Diamagnetic correction = -275×10^{-6}. Calculated from the corrections given in P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers, New York, N. Y., 1956. The diamagnetic correction for Ni(I) was taken to be -15×10^{-6}.