bright blue solutions resulted, while passage through anion resins gave dirty yellow solutions. Aqueous solutions of the material had a dirty yellow color, consistent with the simultaneous presence of yellow $Co(phen)_3^{3+}$, violet *cis*-$Co(phen)_2Cl_2^+$, and pink $Co(H_2O)_6^{2+}$.

Vlcek's Product.—Attempts were made to produce the green compound reported as *trans*-$[Co(bipy)_2Cl_2]Cl \cdot 3H_2O$ in ref 4. Very minute quantities of a green material were isolated but in insufficient quantity for further investigation. Most attempts yielded only the violet *cis* isomer.

Results

The green compound reported as *trans*-$[Co(phen)_2Cl_2]Cl \cdot 2HCl$ by Pfeiffer and Werdelmann[1] is reformulated as $[Co(phen)_3]_2[CoCl_4]_3 \cdot 2HCl$. The green compound reported as *trans*-$[Co(phen)_2Cl_2]^+(H_7O_3)^+Cl^-{}_2$ by Miller and Prince[2] is reformulated as *cis*-$[Co(phen)_2Cl_2][Co(phen)_3][CoCl_4]_2 \cdot 3H_2O$. These new formulations are consistent with evidence presented in the Experimental Section.

Discussion

After completion of this work, Gibson and coworkers[8] reported the preparation of the Pfeiffer and Werdelmann product but gave results differing significantly from ours. Mixtures were obtained when the Pfeiffer and Werdelmann procedure was followed, with *cis*-$[Co(phen)_2Cl_2][CoCl_3(H_2O)][H_{2n}O_n]Cl \cdot (2.5 - n)H_2O$ being a common formulation. Contrary to these results, our product has been shown to contain the *tris* cation by isolation of the corresponding perchlorate derivative (no derivatives were isolated in the Gibson work). In addition there are large differences in the observed C, H, and N values. The product reported as $[Co(phen)_3][phenH][CoCl_4]_2 \cdot HCl$ in ref 8, which most closely resembles our formulation, was not obtained by the exact Pfeiffer and Werdelmann method. Other reaction products given in ref 8 were also obtained by variations in the procedure, and, hence, comparison of these products to our formulation is not valid.

Both *trans*-$[Co(py)_4Cl_2]Cl$ and *trans*-$[Co(en)_2Cl_2]Cl$ are green and previous workers have assigned the *trans* configuration to analogous bipy and phen complexes on this basis. In the two cases reported here the green color results from the simultaneous presence of yellow $Co(phen)_3^{3+}$ and blue $CoCl_4^{2-}$.

It appears from our results and those of others[5,8] that, even though several compounds appear in the literature as containing *trans*-$Co(NN)_2Cl_2^+$ cations of phen and bipy, there is at present no independently substantiated example of such a cation. Rund has shown[9] that phen ligands in such *trans* species experience mutual repulsions by the protons at the 2 and 9 positions and this represents an unfavorable energetic situation in the case of Rh. In the Co case one would expect this repulsion to be even more severe. Hence, if such *trans* cations of Co are ever isolated, it is probable that they will have geometries severely distorted from a regular *trans* arrangement.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation, through the Undergraduate Research Participation Program, for partial support of this work.

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The Reaction between Phosphorus Trichloride and 1,1-Dimethylhydrazine

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In 1961 Holmes[2] reported that PCl_3 reacts with excess H_2NCH_3 to form $P_4(NCH_3)_6$. He assigned this compound a cage structure in which the four phosphorus atoms occupy the corners of a tetrahedron with the NCH_3 groups bridging the edges. As part of an extensive study of the reactions between $R_{3-n}PCl_n$ and methylhydrazines Nielson and Sisler[3] investigated the corresponding reaction between excess $H_2NN(CH_3)_2$ and PCl_3. On the basis of the ratio of phosphorus trichloride used to the hydrazine hydrochloride produced they assumed the reaction to be

$$PCl_3 + 6H_2NN(CH_3)_2 \longrightarrow P\{HNN(CH_3)_2\}_3 + 3H_2NN(CH_3)_2 \cdot HCl \quad (1)$$

An uncharacterized product was postulated to be the trihydrazide, $P\{NHN(CH_3)_2\}_3$. However, if a reaction analogous to the phosphorus trichloride–methylamine reaction is written for the 1,1-dimethylhydrazine case

$$4PCl_3 + 18H_2NN(CH_3)_2 \longrightarrow P_4\{NN(CH_3)_2\}_6 + 12H_2NN(CH_3)_2 \cdot HCl \quad (2)$$

the $PCl_3 : H_2NN(CH_3)_2 \cdot HCl$ ratio of 1:3 is identical with the corresponding ratio for reaction 1. As a similarity in reactivity with PCl_3 between methylhydrazines and corresponding primary amines has previously been noted[4] we decided to reinvestigate the reaction between PCl_3 and $H_2NN(CH_3)_2$ to determine if the trihydrazide was actually produced.

Experimental Section

All manipulations were performed in a vacuum line or under a dry nitrogen atmosphere using standard techniques.[5] Phosphorus trichloride (Matheson Coleman and Bell) and 1,1-dimethylhydrazine (Aldrich Chemical Co.) were distilled immediately before use. All other solvents and reactants were dried and/or purified by appropriate means.

All nmr spectra were recorded in H_2CCl_2 solutions in a Varian A-60 spectrometer at about 35°. Chemical shifts were observed relative to the H_2CCl_2 singlet. The δ values reported in this paper have been converted to a tetramethylsilane reference by

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subtracting 5.30 from the values relative to H_2CCl_2. The mass spectra were run as solid samples on a Hitachi RMU-6D spectrometer. Since peaks were observed at nearly every value of *m/e*, only those whose intensity exceeded 1% of the base peak were considered when interpreting or tabulating the spectra. Infrared spectra were recorded using a Beckman IR-5. Elemental analysis was performed by Galbraith Laboratories, Knoxville, Tenn.

The Reaction between PCl_3 and Excess $H_2NN(CH_3)_2$.—In a vacuum line 4.0 g (0.029 mol) of PCl_3 was distilled into a reaction flask containing a stirring bar. The temperature of the reaction vessel was maintained at −78° and 9.0 g (0.15 mol) of $H_2NN(CH_3)_2$ was allowed to condense into the flask. While stirring, the flask was allowed to warm to room temperature and to remain at this temperature for 0.5 hr to ensure complete reaction. The excess hydrazine was then distilled off, first, from the flask at ambient temperature and, for the last several minutes, at 50°.

The white solid remaining in the reaction flask was transferred to a dry N_2 atmosphere and extracted with 30–60° petroleum ether. A 7.1-g amount (0.074 mol) of $H_2NN(CH_3)_2 \cdot HCl$ was recovered as the petroleum ether insoluble fraction. The petroleum ether was evaporated from the filtrate leaving white, solid $P_4\{NN(CH_3)_2\}_6$ which could be further purified by recrystallization from petroleum ether; mp 46° (final yield: 2.0 g, 0.0042 mol). *Anal.* Calcd for $P_4\{NN(CH_3)_2\}_6$: C, 30.51; H, 7.63; N, 35.59; mol wt 472. Found: C, 30.56; H, 8.15; N, 35.37; mol wt 472 (mass spectra), 495 (cryoscopic in benzene). Major peaks in the ir spectrum: 3110 (s), 2945 (s), 2850 (s), 2730 (m), 2350 (m), 1625 (m), 1460 (m), 1440 (w), 1400 (w), 1298 (m), 1285 (w), 1205 (s), 1158 (m), 1065 (s), 1102 (s), 940 (br), 910 (sh), 800 cm^{-1} (m).

Reaction of PCl_3 with $H_2NN(CH_3)_2$ in 1:3 Molar Ratio.—In a typical experiment 6.0 g (0.10 mol) of $H_2NN(CH_3)_2$ was distilled into a reaction flask containing 5.0 g (0.036 mol) of PCl_3. The temperature was held at −78° throughout this addition. After the initially vigorous reaction subsided, the reaction mixture was carefully warmed to room temperature and was allowed to stand for 30 min at this temperature to ensure complete reaction. Excess or unreacted PCl_3 and/or $H_2NN(CH_3)_2$ was distilled off and the remaining solid was extracted with petroleum ether leaving 5.8 g (0.060 mol) of $(CH_3)NNH_2 \cdot HCl$. The petroleum ether was evaporated from the filtrate leaving 1.5 g (0.0040 mol) of white solid $\{ClPNN(CH_3)_2\}_3$. At room temperature this air- and moisture-sensitive compound decomposes into an uncharacterized yellow mixture within a few hours. Because of this instability good elemental analyses or ir spectra could not be obtained; the compound was characterized by nmr and mass spectroscopy.

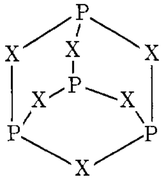
Reaction of $P_4\{NN(CH_3)_2\}_6$ with PCl_3.—Phosphorus trichloride (1.0 g, 0.007 mol) was distilled into a reaction vessel containing a stirred solution of 1.0 g (0.002 mol) of $P_4\{NN(CH_3)_2\}_6$ in about 30 ml of ether at −78°. The solution was warmed to room temperature and stirred for 1 hr. The volatile components were then distilled through cold traps held at −78 and −196°, where excess PCl_3 and solvent ether collected, respectively. No other volatile products were detected. The solid product remaining in the reaction flask was identical with the $\{ClPNN(CH_3)\}_3$ prepared as described above.

Reaction of $\{ClPNN(CH_3)_2\}_3$ with $H_2NN(CH_3)_2$.—Because of difficulties in handling pure samples of $\{ClPNN(CH_3)_2\}_3$, no attempts were made quantitatively to measure amounts in this experiment, although approximate 1-g quantities of $\{ClPNN(CH_3)_2\}_2$ were used. A solution of $\{ClPNN(CH_3)_2\}_3$ in about 30 ml of ether was held at −78° on the vacuum line and several milliliters of $H_2NN(CH_3)_2$ was distilled into the flask. No visible reaction occurred at −78°, but as the mixture was warmed to room temperature, a white precipitate of $(CH_3)_2NNH_2 \cdot HCl$ formed. After 1 hr at room temperature the $(CH_3)_2NNH_2 \cdot HCl$ was filtered off and the ether evaporated on the vacuum line, leaving a white solid identical with the $P_4\{NN(CH_3)_2\}_6$ described above.

Reaction of PCl_3 with $H_2NN(CH_3)_2$ in Less Than 1:3 Molar Ratio.—Using the procedure described for the preparation of $\{ClPNN(CH_3)_2\}_3$, 3.5 g (0.058 mol) of $H_2NN(CH_3)_2$ was condensed into about 30 ml of an ethereal solution containing 4.5 g (0.033 mol) of PCl_3. The resultant $H_2NN(CH_3)_2 \cdot HCl$ (3.4 g, 0.035 mol) was removed by filtration, and the solvent ether was rapidly evaporated from the filtrate leaving 1.8 g (0.0048 mol) of the white solid $Cl_5P_3\{NN(CH_3)_2\}_2$. Decomposition of this product began immediately upon warming to room temperature and we were unable to characterize it completely. The mass spectral molecular weight was 384 [theoretical value for $Cl_5P_3\{NN(CH_3)_2\}_2$, 384], and the relative peak intensities of the parent ions indicated five chlorines. In other preparations mixtures of $Cl_5P_3\{NN(CH_3)_2\}_2$ and $\{ClPNN(CH_3)_2\}_3$ were sometimes obtained. $\{ClPNN(CH_3)_2\}_3$ is also observed as one of the decomposition products of $Cl_5P_3\{NN(CH_3)_2\}_2$.

Results and Discussion

The reaction of PCl_3 with excess $H_2NN(CH_3)_2$ produces $P_4\{NN(CH_3)_2\}_6$. Structurally this product probably resembles the compound formed in the reaction between PCl_3 and H_2NCH_3,[2] that is



where X = NCH_3 in the PCl_3–H_2NCH_3 reaction and X = $NN(CH_3)_2$ in the PCl_3–$H_2NN(CH_3)_2$ reaction.

The ^1H nmr spectrum of $P_4\{NN(CH_3)_2\}_6$, a singlet at δ −2.52 ppm, indicates magnetically equivalent N-methyl groups, as would be expected from the postulated structure if free rotation occurs about the C–N and N–N bonds. The mass spectrum (Table I) indicates

TABLE I

MASS SPECTRUM OF $P_4\{NN(CH_3)_2\}_6$ AT 20 eV

m/e	% Σ_{40}	Possible assignment[a]	*m/e*	% Σ_{40}	Possible assignment[a]
472	1.1	$P_4N_{12}C_{12}H_{36}$	178	5.0	$P_3N_4C_2H_5$
431	0.5	$P_4N_{11}C_{10}H_{33}$	164	1.6	$P_2N_4C_3H_{10}$
430	0.9	$P_4N_{11}C_{10}H_{32}$	148	7.4	$P_2N_4C_2H_6$
429	0.4	$P_4N_{11}C_{10}H_{31}$	138	1.0	$P_3N_3H_3$
414	0.4	$P_4N_{10}C_{10}H_{30}$	137	2.5	$P_3N_3H_2$
402	1.1	$P_4H_{10}C_9H_{30}$	136	2.0	P_3N_3H
343	1.1	$P_4N_8C_7H_{23}$	124	0.9	$P_3N_2H_3$
296	5.0	$P_4N_6C_6H_{16}$, $P_2N_8C_8H_{26}$	123	1.4	$P_3N_2H_2$
281	3.0	$P_3N_7C_6H_{18}$	122	2.0	P_3N_2H
267	0.4	$P_3N_6C_6H_{18}$	105	1.2	$P_2N_2CH_3$
255	1.6	$P_3N_6C_5H_{18}$	104	1.3	$P_2N_2CH_2$
254	1.2	$P_3N_6C_5H_{17}$	89	2.3	$PN_2C_2H_6$
253	0.5	$P_3N_6C_5H_{16}$	60	5.0	$N_2C_2H_8$
252	3.0	$P_3N_6C_5H_{15}$	59	2.0	$N_2C_2H_7$
238	2.5	$P_3N_6C_4H_{13}$, $P_2N_6C_6H_{20}$	58	1.6	$N_2C_2H_6$
237	2.9	$P_3N_6C_4H_{12}$, $P_2N_6C_6H_{19}$	45	7.2	NC_2H_7
222	1.6	$P_3N_6C_3H_9$, $P_3N_5C_4H_{11}$	44	4.5	NC_2H_6
180	3.0	$P_3N_4C_2H_7$	43	1.3	NC_2H_5
179	14.5	$P_3N_4C_2H_6$	42	2.0	NC_2H_4

[a] These assignments have not been confirmed by high-resolution mass spectroscopy; hence some of proposed formulas may be in error.

that fragmentation of this compound occurs largely through cleavage of P–N or N–N bonds. A number of rearrangements obviously take place, but this is not surprising since similar processes are seen in the spectra of a variety of compounds.[6] The parent ion is at *m/e* 472, the molecular weight of the proposed structure from which all the observed fragments could have arisen by a logical fragmentation. With the obvious exception of the N–H vibrations, the ir spectrum of $P_4\{NN(CH_3)_2\}_6$ is quite similar to that of $H_2NN(CH_3)_2$[7] in the 4000- to 1000-cm^{-1} region. Although a detailed ir analysis was not attempted, these data strongly imply that the $NN(CH_3)_2$ moiety retains its identity in $P_4\{NN(CH_3)_2\}_6$. As N–P vibrations are known[8] to occur between 1000 and 600 cm^{-1}, spectral differences between the two compounds should occur in this region. While none of these data, viewed individually, unambiguously demand the proposed structure, a plausible alternative consistent with all of them is difficult to write.

As the relative amount of $H_2NN(CH_3)_2$ used in the reaction is reduced, the composition of the reaction products is also altered. At $PCl_3:H_2NN(CH_3)_2$ ratios close to 1:3 a relatively unstable compound of molecular weight 372 is produced. Relative intensities of 100:97:32:4 for the P, P + 2, P + 4, and P + 6 peaks (P = parent ion) in the mass spectrum (Table II) closely approximate the theoretical values[9] of 100:99.8:31.9:3.5 expected for a molecule containing three chlorines. The fragmentation of this compound largely involves loss of $NN(CH_3)_2$, PCl, or Cl groups. The ^1H nmr spectrum is a singlet, δ −2.95 ppm, indicating magnetically equivalent NCH_3 groups. Although further characterization could not be carried out on the compound due to its instability, these data, combined with elementary valence considerations, imply a cyclic $\{ClPNN(CH_3)_2\}_3$.

A relationship between these two compounds, $P_4\{NN(CH_3)_2\}_6$ and $\{ClPNN(CH_3)_2\}_3$, is clearly indicated by their ready interconvertability

$$P_4\{NN(CH_3)_2\}_6 + 2PCl_3 \longrightarrow 2\{ClPNN(CH_3)_2\}_3$$

$$4\{ClPNN(CH_3)_2\}_3 + 18H_2NN(CH_3)_2 \longrightarrow 3P_4\{NN(CH_3)_2\}_6 + 12H_2NN(CH_3)_2\cdot HCl$$

Evidently though the PCl_3–$H_2NN(CH_3)_2$ system is still more complicated. When the $PCl_3:H_2NN(CH_3)_2$ ratio is reduced below 1:3, another extremely unstable compound, which could only be characterized by its mass spectrum (Table II), was obtained. Its molecular weight of 384 and relative intensities of the P, P + 2, P + 4, P + 6, and P + 8 peaks of 100:160:103:36:6 (theoretical[9] for five chlorines, 100:163:106:34.7:5.7) imply a formula of $Cl_5P_3\{NN(CH_3)_2\}_2$ for which a chain structure can be written: $Cl_2PN\{N(CH_3)_2\}P(Cl)N\{N(CH_3)_2\}PCl_2$.

Even though it has not been possible completely to characterize all the compounds observed to form during the PCl_3–$H_2NN(CH_3)_2$ reaction and the structure of at least $Cl_5P_3\{NN(CH_3)_2\}_2$ is tentative, this system is clearly quite complex. The formation of the moderately stable $P_4\{NN(CH_3)_2\}_6$ is preceded by the production of a series of less stable compounds some of which, at least, are interconvertable into one another. With the exception of $P_4(NCH_3)_6$ production similar behavior has not been reported in the PCl_3–H_2NCH_3 system. In view of the similarities observed here and elsewhere[3,4] between the reactivity of the methylhydrazines and methylamines with PCl_3, it is possible, if not probable, that the reaction of phosphorus trichloride and methylamine is considerably more complex than reports currently available indicate.

TABLE II

MONOISOTOPIC MASS SPECTRA OF $\{ClPNN(CH_3)_2\}_3$ AND $Cl_2PN\{N(CH_3)_2\}P(Cl)N\{N(CH_3)_2\}PCl_2$ AT 20 EV

$\{ClPNN(CH_3)_2\}_3$			$Cl_2PN\{N(CH_3)_2\}P(Cl)N\{N(CH_3)_2\}PCl_2$		
m/e[a]	% Σ_{40}[b]	Possible assignment[c]	*m/e*[a]	% Σ_{40}[b]	Possible assignment[c]
372	4.2	$Cl_3P_3N_6C_6H_{18}$	384	3.1	$Cl_5P_3N_4C_4H_{12}$
314	2.3	$Cl_3P_3N_4C_4H_{12}$	349	1.8	$Cl_4P_3N_4C_4H_{12}$
279	3.3	$Cl_2P_3N_4C_4H_{12}$	306	1.5	$Cl_4P_3N_3C_2H_7$
248	6.2	$Cl_2P_2N_4C_4H_{12}$	260	3.7	$Cl_4P_2N_2C_2H_6$
236	0.4	$P_2N_6C_6H_{18}$	225	5.9	$Cl_3P_2N_2C_2H_6$
213	1.0	$ClP_2N_4C_4H_{12}$	182	2.1	$ClPN_4C_4H_{12}$
191	3.9	$P_2N_5C_4H_{12}$	168	0.7	$ClPN_4C_3H_8$
169	2.4	$ClPN_4C_3H_{11}$	159	11.6	$Cl_2PN_2C_2H_6$
168	5.8	$ClPN_4C_3H_{10}$	147	1.0	$PN_4C_4H_{12}$
155	3.5	$ClP_2N_2C_2H_6$	136	0.4	PCl_3
147	1.7	$PN_4C_4H_{12}$	124	30.4	$ClPN_2C_2H_6$
145	1.0	$PN_4C_4H_{10}$	110	2.8	$ClPN_2CH_4$
136	7.5	PCl_3	101	2.3	Cl_2P
133	10.6	$PN_4C_3H_{10}$	89	5.9	$PN_2C_2H_6$
124	6.7	$ClPN_2C_2H_2$	66	1.6	ClP
110	3.3	$ClPN_2CH_4$	60	0.5	$N_2C_2H_8$
101	8.3	Cl_2P	59	3.5	$N_2C_2H_7$
89	1.4	$PN_2C_2H_6$	58	5.2	$N_2C_2H_6$
60	7.2	$N_2C_2H_8$	44	2.6	NC_2H_6
59	10.2	$N_2C_2H_7$	43	10.0	NC_2H_5
58	2.4	$N_2C_2H_6$	42	2.9	NC_2H_4
45	3.0	NC_2H_7			
44	1.7	NC_2H_6			
43	1.3	NC_2H_5			
42	0.8	NC_2H_4			

[a] *m/e* values are for the ion containing the ^{35}Cl isotope. [b] % Σ_{40} values are summed over all Cl isotopes for the particular ion. [c] While these assignments are tentative, the number of chlorine atoms was confirmed in every case by the intensities of the respective isotope peaks.

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