

Infrared spectral data for 2-(Cl₂B)B₅H₈ (10-cm gas cell equipped with KBr windows): 2592(s), 1785 (w, br), 1395 (m, br), 1335 (w, sh), 1187 (w), 1140 (m), 975 (sh), 937 (s), 885 (s), 839 (sh), 775 (w), 722 (w), 660 (m), 590 (w, br), 448 (w) cm⁻¹.

Reaction of 2-(Cl₂B)B₅H₈ with Diethyl Ether. Into a 9-mm-o.d. tube (as described previously) were condensed at -197 °C 0.2 mmol of 2-(Cl₂B)B₅H₈ and 1 mL of diethyl ether. The tube was warmed to -80 °C, agitated, and then placed in the probe of the NMR spectrometer for ¹¹B analysis. At -80 °C complexation of the ether had already occurred and only the signals of 2-(Cl₂B-OEt₂)B₅H₈ were present in the spectrum.

Reaction of 2-(Cl₂B)B₅H₈ with Bromine. Into a 9-mm-o.d. tube (as described previously) were condensed at -197 °C 0.11 mmol of 2-(Cl₂B)B₅H₈, 1 mL of CH₂Cl₂, and 0.13 mmol of Br₂ (the once fractionated bromine was dried over P₂O₅ at room temperature). The mixture was warmed to -80 °C with agitation and then placed in the NMR probe. At 0 °C the signals of 2-BrB₅H₈¹⁸ began to slowly grow, and after 1.5 h at room temperature the reaction was essentially complete. The color of the solution, which had been previously a very dark orange-red, had faded to a light yellow.

Since immediate assignment of the ¹¹B NMR signals of the products was quite difficult due to extensive peak overlap, the product mixture was fractionated on the vacuum line. When the volatile component was passed through a -63 °C trap, the high-volatility (BCl₃, BBr₃) component could be separated and identified. The low-volatility fraction consisted of 2-BrB₅H₈ (signals at -13.2, -20.9, and -52.9 ppm; lit.¹⁸ ~-11, ~-15, ~-20, and -53.5 ppm) and possibly a small amount of 1-BrB₅H₈ as identified by the presence of signals at -12.6 and -35.9 ppm (lit.¹⁸ -12.5 and -36.1 ppm).

Reaction of 2-(Cl₂B)B₅H₈ with Ethylene: Synthesis of 2-(Cl₂BC₂H₄)B₅H₈. In a typical preparation 0.75 mmol of 2-(Cl₂B)B₅H₈

was condensed at -197 °C into a 22-mm-o.d. tube (as described previously). Above the borane compound were condensed 2 mL of CH₂Cl₂ and 1.33 mmol of C₂H₄. The mixture was then warmed to room temperature, and stirring was commenced. After 2-3 h the solution had turned slightly yellow, but this color did not appear to intensify with prolonged reaction. The stirring was continued for 2 weeks, constantly at room temperature. Then the reactor vessel was connected to the vacuum line and all of the volatiles were condensed into a -197 °C trap. The new compound, 2-(Cl₂BC₂H₄)B₅H₈, was isolated in a pure form by fractional condensation of the volatile component into a -35 °C trap. The compound was a colorless liquid. The ¹¹B NMR spectra of the neat compound or its CH₂Cl₂ solution showed no sign of decomposition after 2 h of standing at room temperature. Yield: 0.14 mmol or 18.6% based on the original amount of 2-(Cl₂B)B₅H₈. The other major identifiable boron-containing product was B₅H₉, which was identified by its ¹¹B NMR spectrum.

Reaction of 2-(Cl₂BC₂H₄)B₅H₈ with THF. A 0.10-mmol sample of 2-(Cl₂BC₂H₄)B₅H₈ was condensed at -197 °C into a 9-mm-o.d. reaction tube (as described previously). Above this compound was condensed 1.5 mL of THF; the mixture was warmed with agitation to -80 °C and then placed into the probe of the NMR spectrometer. At this point the reaction was complete, and quantitative conversion into the THF complex was indicated by the ¹¹B NMR spectrum (see Table I).

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New Chemistry of (Difluoromethyl)phosphines

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The new phosphines (CHF₂)₃P, (CHF₂)₂PI, and CHF₂PI₂ were made in high yields from P₄ and CHF₂I at 190 °C. A low-yield source of CHF₂I was the action of I₂ on MCO₂CHF₂ salts; the new ester CHF₂OC(O)CHF₂ was the major product. Phosphines made from (CHF₂)₂PI were P₂(CHF₂)₄, (CHF₂)₂PPI, and (CHF₂)₂PH; CHF₂PI₂ was converted to CHF₂PH₂ and CHF₂PPI₂. All of these are far less volatile than the analogous CF₃ phosphines; CH...F bonding interaction is suggested. The hybrid diphosphine (CHF₂)₂P-P(CF₃)₂ was formed in equilibrium with P₂(CHF₂)₄ and P₂(CF₃)₄ at 25 °C and recognized by NMR spectroscopy. HCl cleaves it to form primarily (CF₃)₂PH and (CHF₂)₂PPI—necessarily because (CHF₂)₂PH and (CF₃)₂PPI quantitatively exchange H for Cl. Also, HCl easily cleaves P₂(CHF₂)₄ but requires catalysis to cleave P₂(CF₃)₄. Base action by CHF₂ phosphines is shown further by the formation of the nonpolar complexes (CHF₂)₂PH·BH₃, (CHF₂)₂P·BH₃, and P₂(CHF₂)₄·BH₃, but not CHF₂PH₂·BH₃. Analogous is the phosphine oxide (CHF₂)₃PO, made from (CHF₂)₃P by action of NO₂. An attempt to convert (CHF₂)₂PH·BH₃ to [(CHF₂)₂PBH₂]_n was encouraging but inconclusive. The action of Hg on CHF₂PI₂ gave apparent (CHF₂P)_n oligomers.

Phosphines containing the P-CHF₂ linkage are of interest because their chemical and physical properties might not always be predictable from the lore of the CH₃ and CF₃ phosphines. An obvious discrepancy is low volatility; for example, CHF₂PH₂ is less than 1/8 as volatile as CH₃PH₂ or CF₃PH₂, and P₂(CHF₂)₄ is less than 1/50 as volatile as P₂(CF₃)₄. The reason must be a C-H-F hydrogen-bonding effect with Δ*H* about 1-2 kcal—weaker than most recognized hydrogen bonding but stronger than the usual van der Waals effects.

This low volatility is a limiting effect because such air-reactive compounds are best studied by high-vacuum methods, whereby it is possible to work safely and often quantitatively with millimole samples of volatile compounds. But the CHF₂ analogues of P₃(CF₃)₅, [(CF₃)₂PBH₂]₃, and (CF₃P)₄ would not be volatile enough for study by such methods. Nonvolatile mixtures formulated as

[(CHF₂)₂PBH₂]_n and (CHF₂P)_n, made by predictable methods but not resolved into individual compounds, could be confirmed only by their chemistry.

Of the previously described CHF₂ phosphines, some have come from attacks upon (CF₃)₂PH by bases, often retaining CF₃ groups.¹⁻⁵ Others were formed by the basic methanolysis of (CF₃PCF₂)₂, but the resulting mixtures were not always completely resolved.⁶ The present paper describes a more systematic ap-

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proach: the expected formation of $(\text{CHF}_2)_3\text{P}$, $(\text{CHF}_2)_2\text{PI}$, and CHF_2PI_2 from CHF_2I and white phosphorus. This process is just like the synthesis of the analogous CF_3 phosphines and is equally efficient, but a more convenient source of CHF_2I is needed.

Experimental Methods

Techniques. The Stock-type high-vacuum methods here employed have been described in recent related papers.²⁻⁶ For the bomb-tube reactions using P_4 , this hazardous substance was melted in a test tube and drawn into a 4-mm (o.d.) glass tube. The weight of solid P_4 per unit length of tube was determined, so that the desired amount could be cut off with minimal access of air. The resulting glass capsule was dropped through the 5-mm (i.d.) neck of the nitrogen-filled bomb tube, now heated to melt the P_4 out of its capsule. Then the evacuated bomb tube (of heavy-wall Pyrex, 31 mm o.d.) could be supplied with CHF_2I from the vacuum line, sealed off, and heated in a tube furnace.

Instruments. NMR spectra were recorded mostly by an IBM WP-270SY-FT instrument, provided by the National Science Foundation through a departmental instrumentation grant. The chemical shifts (δ) are positive in the upfield direction for ^{11}B from $(\text{CH}_3\text{O})_3\text{B}$, ^{19}F from Cl_3CF , or ^{31}P from H_3PO_4 , but downfield from $(\text{CH}_3)_4\text{Si}$ for ^1H or ^{13}C . J values are in s^{-1} ("Hz"), a cgs unit. A symbol of the type nJ_{XYZ} denotes multiplicity n for coupling of an observed nucleus X to nucleus Z, usually confirmed by mJ_{ZYX} for nucleus X coupling to Z. For convenience in tables, the lower-left subscript n sometimes is attached to the actual number for J . This system obviously is more explicitly informative and less ambiguous than the more common nJ meaning coupling through a chain of $n + 1$ unspecified atoms.

The infrared spectra were recorded mostly by the Perkin-Elmer 281 instrument, or the Beckman IR20A below 600 cm^{-1} . For both, the normal slit width was employed. The results are listed as frequencies (cm^{-1}) with relative intensities in parentheses, calculated as $k = (100/PL) \log(I_0/I)$ for gas pressure P and path length L , both in cm. Thus the intensities for each spectrum relate to all others reported in the same manner.

Sources of Iododifluoromethane

From Iodoform. The Ruff method for HCF_3 (fluorination of HCl_3 by Hg_2F_2)⁷ gives also CHF_2I , but in yields seldom more than 25%, and pure Hg_2F_2 is obtainable only by a meticulous and time-consuming procedure.⁸ Direct mixing of HCl_3 with Hg_2F_2 at 25°C , without an inert diluent, causes spontaneous ignition. Sublimation of the HCl_3 through a bed of Hg_2F_2 (at 120°C or lower) is recommended. Iodination of HCF_3 by passage over hot Al_2I_6 yields only HCl_3 and recovered HCF_3 . The action of IF_5 on HCl_3 ⁹ might be moderated by using a flow process, improving the yield of CHF_2I , or other volatile fluorides might be used.

From Hunsdiecker (Borodin) Decarboxylations.¹⁰ The action of iodine on AgCO_2CF_3 or (recently in this laboratory) $\text{Hg}_2(\text{C}-\text{O}_2\text{CF}_3)_2$ is quantitative for CO_2 and CF_3I —limited only by liquid-solid contact. Accordingly, the same process was tried with the new salts $\text{AgCO}_2\text{CHF}_2$ and $\text{Hg}_2(\text{CO}_2\text{CHF}_2)_2$. Such salts are easily made from the metal oxides; for the reduction to Hg_2^{2+} one shakes with mercury, the excess of which is left behind by dissolving the salt in boiling water; then most of the salt crystallizes on cooling by ice. The last trace is recovered by freezing out the water; as the ice melts on the filter, the crystals remain.

However, neither $\text{AgCO}_2\text{CHF}_2$ nor $\text{Hg}_2(\text{CO}_2\text{CHF}_2)_2$ gave yields of CHF_2I above 25%; the major product was the new ester $\text{CHF}_2\text{OC}(\text{O})\text{CHF}_2$ (Simonini reaction), with far less $(\text{CHF}_2\text{C}-\text{O})_2\text{O}$. Another byproduct contaminating the CHF_2I could be removed by hydrolysis; it may have been $\text{CHF}_2\text{C}(\text{O})\text{F}$.

The anhydride and the ester were identified by the NMR spectra shown in Table I. The ester (found molecular weight 147 vs. calculated 146) showed volatility 6.5 mm at -22.5°C , 32.3 mm at 0°C , and 110.1 mm at 20.9°C , suggesting $\log P$

Table I. NMR Data for the Hunsdiecker Products

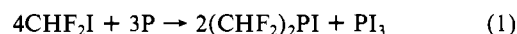
	CHF ₂ I	(CHF ₂ CO) ₂ O ^a	CHF ₂ OC(O)CHF ₂ ^b	
			OCHF ₂	CCHF ₂
δ _H	6.83	6.08	7.280	6.170
³ J _{HCF}	56.1	52.6	69.3	52.4
δ _F	67.2	128 ^c	92.49	129.13
² J _{FCH}	56.1	53	69.3	52.4
δ _C ^d		106	105.2	111.9
³ J _{CF}		247	248	263
² J _{CH}		194	195	230

^aC=O carbon at $\delta = 166.5$ (downfield of Me_4Si); ³J_{COCF} = 29, ²J_{COCH} = 5.3. For the free acid, $\delta_{\text{H}} = 11.25$. ^bC=O carbon at $\delta = 158.5$; ³J_{COCF} = 31 (ragged peaks; ³J_{CCF} not recognizable). ^cT60 instrument. ^dJEOL FX 90Q instrument, with automatic NOE.

= $7.9114 + 1.75 \log T - 0.007T - 2391/T$ (bp 64°C ; Trouton constant 25.1 eu). Such an abnormal result would correlate with strong molecular forces.

Main Synthesis of (Difluoromethyl)phosphines

The addition of CHF_2I to P_4 occurred in sealed heavy-wall Pyrex tubes at $187\text{--}195^\circ\text{C}$. These conditions were essentially the same as for the analogous reaction with CF_3I . The plan was to maximize the yields of $(\text{CHF}_2)_2\text{PI}$: no iodine was used, and in most experiments the P_4 exceeded the amount required by the equation



but the excess was not enough to maximize the yield of $(\text{CHF}_2)_3\text{P}$.

Table II shows the stoichiometry of four such experiments. In each case the unused CHF_2I was isolated by repeated fractional condensation through a U-tube at -78.5°C . The products of experiment 1 were not directly isolated but were determined by use of mercury, leading to easy separation of $(\text{CHF}_2)_3\text{P}$ from the resulting $\text{P}_2(\text{CHF}_2)_4$; then the presumed $(\text{CHF}_2\text{P})_n$ was treated with HCl to produce CHF_2PCl_2 and CHF_2PH_2 , determining the amount of CHF_2P material. These products were not easily separated but were easily recognized by their NMR spectra.

The recovery of CHF_2 groups as phosphines ranged from 67 to 82% (experiment 3a). It is assumed that the loss may have been as $(\text{CHF}_2\text{P})_n$, not recoverable by action of HCl on the solid mass. It might be recovered by action of iodine to make CHF_2PI_2 , but this has not been attempted.

The volatile products of experiments 2–4 were isolated by repeated use of a column with the reflux temperature maintained by frequent addition of solid CO_2 to hexane. The intermediate fractions were subjected to fractional condensation. The process was tedious on account of the strong H...F attraction between different molecules. Individual characterizations are as follows.

Tris(difluoromethyl)phosphine. The volatility of $(\text{CHF}_2)_3\text{P}$ (19 mm at 0°C and 63 mm at 22°C), extrapolated with the expected curvature, indicates a normal boiling point near 86°C . Its vapor-phase molecular weight was determined as 185 (calculated 184). The NMR data, whereby it was previously recognized in a mixture,⁶ appear in Table III and again in Table IV for purposes of comparison.

The easily observable infrared frequencies of $(\text{CHF}_2)_3\text{P}$ are listed (cm^{-1} , with relative intensities in parentheses) as follows: 2965 (1.5), 1336 (2.4), 1300 (8.4), 1095 (41), 1062 (31), 787 (1.0), 749 (0.77), 729 (1.3), 677 (0.78), 568 (0.28), 553 (0.25), 477 (0.2), 425 (1.1), and 397 (1.3). Here the ν_{asym} peaks for C–F (in and out of phase, at 1300 and 1336) are well separated from ν_{sym} (1062 and 1095), in contrast to PCF_3 ν values usually in the 1110–1190 range. The 1336 peak may include C–H bending—not seen otherwise. Correlated with ν_{sym} are overtones and combinations appearing as a weak and unresolved band near 2140. The CF δ peaks in the range 553–787 are not so easily assigned to specific modes. The frequencies below 500 probably concern P–C stretching modes, again with specific assignments uncertain.

Bis(difluoromethyl)iodophosphine. The new compound $(\text{CHF}_2)_2\text{PI}$ can be purified by repeated high-vacuum fractional con-

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Table II. Stoichiometry of CHF_2 Phosphine Syntheses

expt no.	amt of CHF_2I , mmol		amt of P_4 , g	heat		amt of products, mmol		
	used	consumed		time, h	temp, °C	$(\text{CHF}_2)_3\text{P}$	$(\text{CHF}_2)_2\text{PI}$	CHF_2PI_2
1	6.487	6.40	1.0	72	195	1.082	0.672	0.141
2	13.90	13.55	0.63	24	190	1.245	1.942	1.560
3	16.48	12.81	1.1	40	193	0.830	2.680	0.595
3a	3.67 ^a	3.02	(res)	72	195	0.262	0.824	0.236
4	13.897	9.17	1.1	69	187	(0.611)	1.662	<i>b</i>
4a	4.729 ^b	3.987	(res)	96	190	0.897	1.355	0.548

^aThe three products of experiment 3 were removed, and the process was continued with the remaining reactants in the same tube. ^bHere only the product $(\text{CHF}_2)_2\text{PI}$ was removed, and the rest was returned to the same tube for further action. The purpose here was to maximize $(\text{CHF}_2)_2\text{PI}$ at the expense of $(\text{CHF}_2)_3\text{P}$ and CHF_2PI_2 .

Table III. Comparison of NMR Data for Monophosphines

	$(\text{CHF}_2)_3\text{P}$	$(\text{CHF}_2)_2\text{PH}^a$	$(\text{CHF}_2)_2\text{PCl}$	$(\text{CHF}_2)_2\text{PI}$	$\text{CHF}_2\text{PH}_2^b$	CHF_2PCl_2	CHF_2PI_2
δ_{HC}	6.2	6.095	5.51	5.0	6.322	5.25	5.0
$^3J_{\text{HCF}}$, s ⁻¹	50.3	50.7	50.9	51.7	51.6	51.8	52.4
$^2J_{\text{HCP}}$, s ⁻¹	15.3	15.5	see text	19.4	18.0	15.2	22.9
δ_{F}	120.2	113.6 ^c	124.4 ^c	115.4 ^c	105	125	110
$^2J_{\text{FCP}}$, s ⁻¹	104.6	93.8	104.6	101.5	112.7	94.0	97.4
$^2J_{\text{FCH}}$, s ⁻¹	50.9	51	51	50.1	51.5	51.1	51.3
$^nJ_{\text{FCPH}}$, s ⁻¹		2 16.5	2 20.3				3 20.4
$^nJ_{\text{FCPCH}}$, s ⁻¹	3 4.25 ^d	2 4.6	2 4.4	see text	see text		
$\Delta\delta_{\text{AB}}$, ppm		0.8360	3.5861	4.0692			
$^2J_{\text{FCF}}$, s ⁻¹		329	335	321			
I_0/I_i							
obsd		0.1	0.5	0.55			
calcd		0.08	0.49	0.54			
δ_{P}	23.5	62	-46	0.6	132	-134	-69
$^nJ_{\text{PH}}$, s ⁻¹		2 214			3 199.5		
$^nJ_{\text{PCF}}$, s ⁻¹	7 105	3 93.8	3 104.6	5 107.6	3 87.8	3 121.2	3 86.4
$^nJ_{\text{PCH}}$, s ⁻¹	4 15.0	3 15.5	3 18.7	3 19.4	2 18.2	(14?)	2 22.7

^a $\delta_{\text{HP}} = 3.516$; $^2J_{\text{HP}} = 213.6$; $^3J_{\text{HPCF}} = 16.46$ or 20.35 ; $^3J_{\text{HPCH}} = 2.95$ ($^2J_{\text{HCPH}} = 2.95$). ^b $\delta_{\text{HP}} = 2.9123$; $^2J_{\text{HP}} = 199.5$; $^3J_{\text{HPCF}} = 20.38$; $^2J_{\text{HPCH}} = 3.19$ ($^3J_{\text{HCPH}} = 3.18$). ^cCenter of the AB spectrum. ^d $^5J_{\text{HPCF}} = 4.33$.

Table IV. NMR Comparison of Phosphines and Their Adducts

	$(\text{CF}_3)_3\text{P}$	$(\text{CF}_3)_3\text{PO}$	$(\text{CHF}_2)_3\text{P}$	$(\text{CHF}_2)_3\text{PO}$	$(\text{CHF}_2)_3\text{PBH}_3$
δ_{H}			6.2	5.0	
$^3J_{\text{HCF}}$, s ⁻¹			50.3	48.25	
$^2J_{\text{HCP}}$, s ⁻¹			15.3	27.65	
J_{HPCF} , s ⁻¹			4.33	4.9	
δ_{F}		52	67.9	120.2	133.3
$^2J_{\text{FCP}}$, s ⁻¹		85.7	113.75	104.6	77.7
$^2J_{\text{FCH}}$, s ⁻¹				50.9	48.25
$^3J_{\text{FCPCH}}$, s ⁻¹				4.25	4.7
δ_{P}		2.5	-3.4	23.5	-15.8
J_{PCF} , s ⁻¹		85	113.7	105	77.6
$^4J_{\text{PCH}}$, s ⁻¹				15.0	27.65

densation, using traps at -10 and -30 °C. The pure product is colorless but may turn yellow within 1 week or so, as it progresses toward equilibrium with I_2 and $\text{P}_2(\text{CHF}_2)_4$, probably more slowly than the similar action of $(\text{CF}_3)_2\text{PI}$. Rapidly reactive toward mercury, its volatility could be observed only roughly, as 4 mm at 0 °C, about one-tenth that of $(\text{CF}_3)_2\text{PI}$.

The NMR data in Table III indicate the AB character of F in $(\text{CHF}_2)_2\text{PI}$, with further splitting by P and H; then each of the 16 clusters has irregular fine structure in the manner of Figure 2 of ref 6. As in that case, each of the four main branches has the first and third clusters just alike, and so also the second and fourth. It is interesting that the ^{19}F spectrum of "neat" $(\text{CHF}_2)_2\text{PI}$ failed to show the cluster fine structure, which was well resolved in the spectrum of a $(\text{CHF}_2)_2\text{PI}$ impurity in CHF_2PI_2 , and then the main J values were lower: $^2J_{\text{FCP}} = 91.6$ or 95.8 and $^2J_{\text{FCH}} = 50.4$ or 51.1 . It appears that intermolecular forces affect coupling and resolution.

(Difluoromethyl)diiodophosphine. The new compound CHF_2PI_2 could be distilled only very slowly in the vacuum line at 25 °C; as expected, it is less volatile than CF_3PI_2 . Like that analogue, it forms intensely yellow droplets having a fairly steep contact angle with glass. Its NMR spectra (Table III) indicate simplicity.

The ^{19}F peaks are very sharp, apparently little affected by the iodine quadrupole.

Derived Monophosphines

Bis(difluoromethyl)phosphine. Pure $(\text{CHF}_2)_2\text{PH}$ surely could be made directly from $(\text{CHF}_2)_2\text{PI}$ with HI and Hg, but material was conserved by first making $\text{P}_2(\text{CHF}_2)_4$ and characterizing it and then converting 0.435 mmol of this, by action of excess HI and Hg, to 0.866 mmol of $(\text{CHF}_2)_2\text{PH}$ (99.5% yield). This was easily purified by high-vacuum distillation.

The vapor density of pure $(\text{CHF}_2)_2\text{PH}$ (at 200 mm pressure) gave the molecular weight as 134.5 (calculated 134.0). Its volatility (21.4 mm at -22.6 °C, 79 mm at 0 °C, and 131 mm at 10.1 °C) indicated $\log P = 6.6605 + 1.75 \log T - 0.0066T - 1973/T$ (bp 54 °C; Trouton constant 21.04 eu). Its infrared frequencies are 2955 (1.3), 2320 (1.6), 1329 (3.8), 1307 and 1302 (7.3), 1090 and 1085 (35, with shoulders down to 1062), 896 and 892 (2.4), 860 (1.6), 812 (0.5), 730 (0.65), 652 (0.65), and 541 (3.9). Most of the peaks were complicated by incipient finer structure, not quite resolved into P, Q, and R branches.

The ^1H NMR spectrum of the CHF_2 group here (Table III) failed to show different geminal F atoms, but their AB character

was apparent from the ^{31}P spectrum: the two ${}_3J_{\text{PCF}}$ values aided the sorting out of the badly entangled ^{19}F spectrum. The two CHF_2 groups seemed to be magnetically equivalent, showing the same AB pattern for the geminal F atoms.

Bis(difluoromethyl)chlorophosphine. The compound $(\text{CHF}_2)_2\text{PCl}$, previously made from $\text{CH}_3\text{OP}(\text{CHF}_2)_2$,⁶ now has been made more directly, from 0.54 mmol of $(\text{CHF}_2)_2\text{PI}$ with 300 mg of HgCl_2 , heated in a 15-mL sealed tube for 112 h at 83 °C. The yield was 0.49 mmol, easily purified.

The very strange ^1H NMR spectrum of $(\text{CHF}_2)_2\text{PCl}$ has been described as a triplet of doublets, with the three doublets all showing different fine structure.⁶ It must be added that each member of the central doublet shows the following relative frequencies (and heights): 0 (9), 2.315 (sh, 11), 4.219 (broad, 22), and 7.037 (13). The proton coupling to two kinds of F atoms would be part of the explanation, but not enough to explain the obvious lack of symmetry.

The ^{19}F spectrum of this compound now has been recorded with higher resolution; cf. Table III. The fine structure now looks more like Figure 2 of ref 6, with similar alternating patterns. The spacings vary from 2 to 6 s^{-1} .

(Difluoromethyl)phosphine. Pure CHF_2PH_2 was made directly from 0.549 mmol of CHF_2PI_2 with excess HI and Hg. High-vacuum fractional condensation (through -95 °C; trapped at -105 °C) gave 0.511 mmol of the final product (93% yield); molecular weight 85 (calculated 84). Its volatility (4.65 mm at -79.2 °C, 29.5 mm at -56.4 °C, 264 mm at -18.15 °C, and 602 mm at 0 °C) suggests $\log P = 5.3785 + 1.75 \log T - 1501.5/T$ (bp 5.8 °C; Trouton constant 21.7 eu).

The infrared spectrum of CHF_2PH_2 showed small-molecule complexity, with PQR structure indicated by complex peaks, but not resolved. The easily observable frequencies were 2965 (0.6), 2946 (0.9), 2306 (0.7), 1331-1291 (1.4, five peaks), 1229 (0.25), 1185 (0.4), 1154 (0.3), 1114-1038 (1.5), 902 (0.56), 896 (0.86), 887 (0.88), 882 (0.78), 815 (0.86, broad), 536Q (0.57), 460 (0.08), 405 (0.12), and 350 (0.7, broad). The C-F stretching frequencies are unusually weak and not easily sorted out from C-H and P-H bending. Also P-C stretching is far less intense than in most P-CF_3 compounds and is accordingly difficult to assign.

The ^1H , ^{19}F , and ^{31}P NMR spectra of CHF_2PH_2 proved to be relatively simple; cf. Table III.

(Difluoromethyl)dichlorophosphine. Heating of 0.82 mmol of CHF_2PI_2 with excess HgCl_2 in a 10-mL sealed tube (90 h at 80 °C) yielded 0.65 mmol of CHF_2PCl_2 (79%), purified by fractional condensation (traps at -90 and -70 °C). Its vapor-phase molecular weight was 154 (calculated 153); the ^{19}F NMR spectrum (Table III) showed 0.35% of $(\text{CHF}_2)_2\text{PCl}$ impurity. Quadrupole broadening affected the ^{31}P spectrum. The volatility of CHF_2PCl_2 (3.2 mm at -45.7 °C, 15.4 mm at -22.6 °C, 57 mm at 0 °C, and 161 mm at 21.7 °C) suggests $\log P = 4.9598 + 1.75 \log T - 0.00375T - 1760/T$ (bp 63 °C; Trouton constant 21.6 eu).

The major infrared peaks of CHF_2PCl_2 appeared at 2955 (1.4), 1287 (sh, 4.6), 1282 (5.3), 1072 (60), 1122 (sh, 2.7), 736 (2.4), 585 (0.2), and 517 (10); P-Cl and P- CHF_2 stretching may be superposed.

It is possible to convert CHF_2PCl_2 to CHF_2PH_2 by action of HI and Hg, but this process is less direct and less efficient than the CHF_2PI_2 -HI-Hg method. A mixture of 0.33 mmol of CHF_2PCl_2 and 1.65 mmol of HI, shaken with mercury until all HI was gone, gave only 0.60 mmol of HCl (expected 0.66 mmol) and 0.26 mmol (79%) of impure CHF_2PH_2 .

New Diphosphines

Tetrakis(difluoromethyl)diphosphine. The colorless liquid $\text{P}_2(\text{CHF}_2)_4$, made by the action of mercury on $(\text{CHF}_2)_2\text{PI}$, was easily purified, with volatility 0.4 mm at 0 °C and 2.2 mm at 24 °C; its normal boiling point probably is close to 170 °C. Its ^1H and ^{19}F NMR spectra appear in Figure 1. The ^{31}P NMR spectrum shows a normal base line only when ^1H is decoupled, then showing a quartet of doublets and a triplet of triplets, both centered at $\delta = 31.5$, with approximately equal total intensities. The apparent coupling constants are ${}_4J = 110.4$, ${}_2J = 15.0$, ${}_3J$

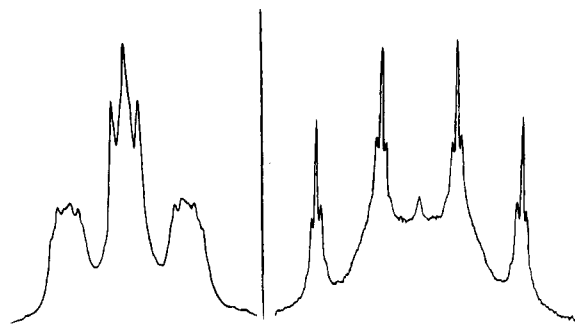


Figure 1. The ^1H (left) and ^{19}F (right) NMR spectra of $\text{P}_2(\text{CHF}_2)_4$. For ^1H , $\delta = 6.3$ (${}_3J_{\text{HCF}} = 49 \text{ s}^{-1}$). The central triplet (${}_3J = 11$) presumably is composite, as the outer clusters must be. The ^{19}F spectrum ($\delta = 112$) almost seems simple, with ${}_2J_{\text{FCP}} = 111 \text{ s}^{-1}$, ${}_2J_{\text{FCH}} = 51.7 \text{ s}^{-1}$, and (less assignable) ${}_3J = 3.64 \text{ s}^{-1}$. However, the central peak indicates second-order character, more complex than that of $\text{P}_2(\text{CF}_3)_4$.¹¹

$= 110.3$, and ${}_3J = 26.0$; cf. ${}_2J_{\text{FCP}} = 111$. However, these are not normal multiplets: for the quartet the relative intensities are 1:5:5:1, and for the secondary triplet, 1:4:1. The peaks have half-height widths in the range 5-7 s^{-1} , suggesting much superposition of fine splittings. Without the decoupling, the same features can be seen, but the irregular clusters ride on a broad mound accounting for about two-thirds of the total intensity. Computer simulation of such a system might be very difficult even if full resolution could be achieved.

Unlike $\text{P}_2(\text{CF}_3)_4$, this diphosphine is easily cleaved by HCl without catalysis, as expected in view of more strongly basic phosphorus atoms. A nearly pure 0.36-mmol sample consumed 0.34 mmol of HCl during 16 h in a closed 10-mL tube at 25 °C, yielding 0.67 mmol of mixed $(\text{CHF}_2)_2\text{PCl}$ and $(\text{CHF}_2)_2\text{PH}$. Not easily separable, these were identified by their NMR spectra.

A New Hybrid Diphosphine. The diphosphine $(\text{CHF}_2)_2\text{PP}(\text{C-F}_3)_2$ was made from 0.247 mmol of $\text{P}_2(\text{CHF}_2)_4$ and 0.268 mmol of $\text{P}_2(\text{CF}_3)_4$, approaching equilibrium for P-P bond exchange during 3-5 days at 25 °C, in a very small sealed glass tube allowing only minimal vapor-phase escape for the more volatile $\text{P}_2(\text{CF}_3)_4$. The product was isolated after each of four such equilibrations; then an equilibration from the opposite direction (disproportionation) confirmed that K is not far from 1. After the original four equilibrations, the yield of the hybrid was 0.425 mmol (87%), that of the remaining $\text{P}_2(\text{CHF}_2)_4$ was 1%, and that of $\text{P}_2(\text{CF}_3)_4$, 9%. The deficiency may be in part attributable to a catalytic scrambling of P-C bonds, indicated by products volatile at -78 °C. One such product may have been $(\text{CF}_3)_3\text{P}$, formed by a process like that which led to the first observation of $(\text{CHF}_2)_3\text{P}$.⁶

The volatility of the pure hybrid diphosphine (4.0 mm at 0 °C, 8.0 mm at 10.2 °C, and 15.3 mm at 21.2 °C) suggests the equation $\log P = 7.0349 + 1.75 \log T - 0.006T - 2474/T$ (bp 116.4 °C; Trouton constant 22.8 eu), the high curvature of which would relate to the suggested H...F attraction.

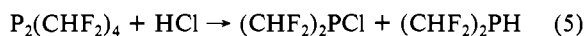
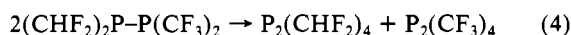
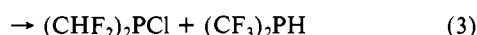
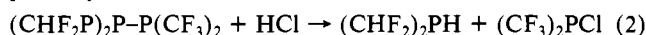
The NMR spectra seemed simple. For ^1H , $\delta = 5.85$ (${}_3J_{\text{HCF}} = 50.5$; ${}_2J_{\text{HCP}} = 21.2$); finer structure (${}_3J$ near 3) could be ascribed to mixing of ${}_3J_{\text{HPCF}}$ and ${}_2J_{\text{HCP}}$; cf. the ^{31}P data.

The ^{31}P spectrum of the $(\text{CHF}_2)_2\text{P}$ group, at $\delta = 27.5$ (${}_2J_{\text{PP}} = 217.9$; ${}_5J_{\text{PCF}} = 98.4$; ${}_3J_{\text{PCH}} = 21.25$; ${}_7J_{\text{PPCF}} = 9.1$), was not disturbed by the $\text{P}_2(\text{CHF}_2)_4$ impurity at 31.5 ppm. Neither in this nor in the ^{19}F spectrum was it possible to find any AB difference between F atoms. For the $\text{P}(\text{CF}_3)_2$ group, $\delta = 10.6$ (${}_2J_{\text{PP}} = 218.0$; ${}_7J_{\text{PCF}} = 71.8$; ${}_5J_{\text{PPCF}} = 18.5$; ${}_3J_{\text{PPCH}} = 2.95$), with only the outermost downfield cluster disturbed by $\text{P}_2(\text{CF}_3)_4$ at $\delta = 8.4$.

The ^{19}F spectrum of this diphosphine ($\delta = 47.1$ for CF_3 and 112.5 for CHF_2) was disturbed by superposition by the unavoidable impurities $\text{P}_2(\text{CF}_3)_4$ and $\text{P}_2(\text{CHF}_2)_4$, at $\delta = 46.5$ and 112. However, the major J values from the other nuclei are roughly confirmed.

HCl Cleavage of the Hybrid Diphosphine. Earlier results with the hybrid diphosphine $(\text{CH}_3)_2\text{P-P}(\text{CF}_3)_2$ ¹² would suggest that

HCl cleavage of $(\text{CHF}_2)_2\text{P}-\text{P}(\text{CF}_3)_2$ would favor formation of $(\text{CF}_3)_2\text{PH}$ and $(\text{CHF}_2)_2\text{PCl}$. In fact, these are almost the only products, despite the smaller difference in electronic conditions for the two phosphorus atoms. The actual experiment may have been complicated by multiple reaction paths; the parallel processes probably were



with $\text{P}_2(\text{CF}_3)_4$ not expected to resist a catalytic environment.⁴

The experiment employed 0.336 mmol of $(\text{CHF}_2)_2\text{P}-\text{P}(\text{CF}_3)_2$ and 0.491 mmol of HCl, heated for 39 h in a sealed tube at 72 °C. Then a rough analysis, including vacuum-line separations, NMR intensity comparisons, and molecular weights of binary mixtures, indicated the following mmol quantities in the final mixture: HCl, 0.236 (used, 0.255); $(\text{CHF}_2)_2\text{P}-\text{P}(\text{CF}_3)_2$, 0.046 (used, 0.290); $(\text{CF}_3)_2\text{PH}$, 0.145; $(\text{CHF}_2)_2\text{PCl}$, 0.128; $(\text{CF}_3)_2\text{PCl}$, 0.007; $(\text{CHF}_2)_2\text{PH}$, 0.024; $\text{P}_2(\text{CF}_3)_4$, 0.034; $\text{P}_2(\text{CHF}_2)_4$, 0.037.

The earlier cleavage of $(\text{CH}_3)_2\text{P}-\text{P}(\text{CF}_3)_2$ was assumed to begin with a protonic attack at the more basic P atom in the manner of reaction 2, followed by a bond exchange like reaction 3, which would be caused by an increase in total bond energy.¹² The irreversibility of the present reaction 3 was not quite assured by these results, but the survival of traces of $(\text{CF}_3)_2\text{PCl}$ and $(\text{CHF}_2)_2\text{PH}$ could be due to their late formation in an incomplete reaction 1. For a more direct test, 0.223 mmol each of $(\text{CF}_3)_2\text{PCl}$ and $(\text{CHF}_2)_2\text{PH}$, left for 17 h at 25 °C in a Wilmad WGS-5BL insert tube, showed complete conversion; only $(\text{CHF}_2)_2\text{PCl}$ and $(\text{CF}_3)_2\text{PH}$ could be seen in the ¹⁹F NMR spectrum.

Exploration of Borane(III) Complexes

The study of the many possible BH_3 complexes of the CHF_2 phosphines would be a large separate project, here only briefly pursued. Most of them should be of the slowly formed nonpolar type, like BH_3CO or BH_3PF_3 , wherein relatively high volatility and poor hydridic reactivity correlate with a weak electron-dative σ bond, the polarity of which is compensated by π return bonding by B-H electrons.¹³ The BH_3 complexes here were not separable from the free phosphines, but their formation was clearly demonstrated by their NMR spectra—especially the ¹¹B quartets in the region of $\delta = 64$ upfield of methyl borate. The ³¹P spectra were strongly confirmatory, for the δ values were far downfield of the free phosphines, as expected when the phosphorus atom becomes quaternary.

Bis(difluoromethyl)phosphine-Borane(III). The most stable BH_3 complex here observed was $(\text{CHF}_2)_2\text{PH}\cdot\text{BH}_3$, formed when 0.400 mmol of $(\text{CHF}_2)_2\text{PH}$ and 0.211 mmol of B_2H_6 were kept together in a small sealed tube for 1 h at 0 °C. Its ¹¹B NMR spectrum appeared at $\delta = 64.6$ ($2J_{\text{BH}} = 105$). The ¹⁹F spectrum (with no AB character) was shifted upfield to $\delta = 123.4$ ($2J_{\text{FCP}} = 64$; $2J_{\text{FCH}} = 49.3$; $2J_{\text{FCPH}} = 9.7$; $2J_{\text{FCPC}} = 1.4$). The ¹H spectrum showed the BH_3 group in its usual region: $\delta = 0.13$ with $J = 102$ for the 1:1:1:1 quartet. The CH and PH protons could not be sorted out from the free ligand. The ³¹P spectrum at $\delta = -7.7$ appeared as a very poorly resolved quintet ($3J_{\text{PCF}}$ underestimated as 59). The relative intensities of ligand *vs.* complex indicated approximately a 2:1 ratio, roughly consistent with the ¹⁹F spectrum of the mixture.

Very different is CHF_2PH_2 , which failed to attach a BH_3 group. The reason is far from simple: less electron withdrawal from P would allow better base action, but the return π bonding would be weaker and each P-H bond has a weakening effect; but steric interference would be less.

The Diphosphine Complex. In a WGS-5BL NMR insert tube at 25 °C, 0.286 mmol of $\text{P}_2(\text{CHF}_2)_4$ with 0.303 mmol of B_2H_6

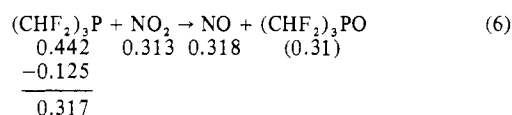
showed the BH_3 quartet at $\delta = 62$ ($J = 107$). The excess B_2H_6 was seen as usual at $\delta = 1.1$. This diborane was removed by passage through a U-trap at -78 °C; 0.259 mmol recovered (85%). However, the dissociation of the complex yielded only 0.18 mmol of B_2H_6 —41% of the expected amount. The deficiency might be explained by the formation of boron compounds showing two very small triplets at $\delta = 26$ ($3J = 130$) and $\delta = 31.8$ ($3J = 153$)—suggestive of possible $(\text{CHF}_2)_2\text{PBH}_2$ oligomers which might have been formed by BH_3 cleavage of the P-P bond; cf. Possible Oligomers.

The Tris(difluoromethyl)phosphine Complex. The initial experiment employed 0.156 mmol of $(\text{CHF}_2)_3\text{P}$ with 0.118 mmol of B_2H_6 , of which only 0.006 mmol was absorbed during 15 h in a 10-mL sealed tube at 0 °C. The usual BH_3 NMR quartet was barely observable at $\delta = 65.2$, with poor resolution. For more effective complex formation, 0.294 mmol of $(\text{CHF}_2)_3\text{P}$ and 0.147 mmol of B_2H_6 were kept in a WGS 5BL insert tube for 1 h at -20 °C, then showing the ¹⁹F NMR spectrum of the complex (cf. Table IV) with intensity roughly half that of the free ligand. This intensity ratio was unchanged at -40 °C, possibly because the expected shift of equilibrium was too slow. It is presumed that $(\text{CHF}_2)_3\text{P}\cdot\text{BH}_3$ is less stable than $\text{P}_2(\text{CHF}_2)_4\cdot\text{BH}_3$, but different rates of equilibration might lead to a false comparison.

The ³¹P NMR spectrum of $(\text{CHF}_2)_3\text{P}\cdot\text{BH}_3$ at -20 °C is compared with others in Table IV. Its coupling structure was unresolvable.

Tris(difluoromethyl)phosphine Oxide. Phosphine oxides may be regarded as another (far more stable) type of P-X σ -dative bonding with π return and so may be compared with phosphine-BH₃ complexes.

The quantitative oxidation of $(\text{CHF}_2)_3\text{P}$ by NO_2 proved to be considerably faster than the similar oxidation of $(\text{CF}_3)_3\text{P}$.¹⁵ It was complete after a 1-h warming from -78 to -20 °C. The millimole stoichiometry



indicated the formula, confirmed by the NMR spectra (Table IV). However, low volatility made it difficult to determine the yield by transferring the sample by sublimation to a weighing bulb.

The oxidation of $(\text{CHF}_2)_3\text{P}$ by NO proved to be very slow at 25 °C, but when carried forward at 110 °C (16 h), the reaction proved to be very complex, with disproportionation of some of the NO to NO_2 and N_2 and formation of a nonvolatile oil. The recoverable yield was 51%, with roughly equimolar N_2 . Unlike the oxidation of $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$ by NO,¹⁶ this process yielded no trace of N_2O .

The new phosphine oxide $(\text{CHF}_2)_3\text{PO}$ melts sharply at 32 °C. It is only slowly sublimable under high vacuum at 25 °C, in dramatic contrast to $(\text{CF}_3)_3\text{PO}$ (volatility 580 mm at 25 °C).¹⁵ However, much of the contrast is due to the unexpectedly high volatility of $(\text{CHF}_2)_3\text{PO}$, apparently due mostly to an almost perfect balance of bond polarities: the dipole in the P→O σ -dative bond may be neatly balanced by that of the return π bonding. In $(\text{CHF}_2)_3\text{PO}$ the P→O dative bond would be stronger and more polar, while the return π bonding would be less effective. It is difficult to decide whether $\text{CH}\cdots\text{O}$ or $\text{CH}\cdots\text{F}$ hydrogen bonding is the primary additional cause of low volatility.

The NMR comparisons in Table IV show interesting trends: bonding of O or BH_3 to P moves δ_{F} upfield but δ_{P} downfield. Also, J_{FCH} (J_{HCF}) is lowered by about 2 s⁻¹ from the very consistent 50–52 range seen for almost all free CHF_2 phosphines.

Possible Oligomers

The Phosphinoboron Type. A 2:1 mixture of $(\text{CHF}_2)_2\text{PH}$ and B_2H_6 was heated in a sealed 120-mL bulb for 15 h at 77 °C, after

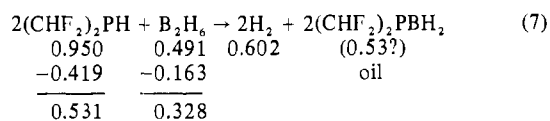
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minimal evolution of H₂ at 25 °C. Equation 7, with millimole



stoichiometry, describes the result. Here the excess consumption of B₂H₆ (0.0625 mmol), yielding 0.071 mmol of excess H₂, may be due to decomposition of B₂H₆.

The oil might be a mixture of (CHF₂)₂PBH₂ oligomers, none of which could be distilled off under high vacuum at 100 °C. However, it did absorb 0.455 mmol of (CH₃)₃N during 20 min at 100 °C—a result possibly analogous to the formation of the monomer complex (CH₃)₃N·(CF₃)₂PBH₂ (and longer chains) from (CH₃)₃N and [(CF₃)₂PBH₂]₃.¹⁴ This subject seems worthy of further study.

Possible (CHF₂P)_n Oligomers. A 0.690-mmol sample of CHF₂PI₂ was completely consumed by repeated distillation at

minimal pressure over droplets of mercury. There was no product appreciably volatile at 25 °C, but a slight sublimate came off under high vacuum at 100 °C; this could be (CHF₂P)_n with *n* minimal. Action upon the whole product by HI produced volatile material, converted by HI and Hg to 0.324 mmol of nearly pure CHF₂PH₂, just as expected if the initial product were (CHF₂P)_n.

Acknowledgment. Thanks are due to Allan Kershaw for the ¹³C NMR spectra and to Dr. K. L. Servis for good advice.

Registry No. (CHF₂)₃P, 94110-53-9; (CHF₂)₂PI, 97523-67-6; CHF₂PI₂, 97523-68-7; CHF₂I, 1493-03-4; P, 7723-14-0; (CHF₂)₂PH, 97523-69-8; P₂(CHF₂)₄, 97523-70-1; (CHF₂)₂PCL, 94110-56-2; HgCl₂, 7487-94-7; CHF₂PH₂, 97523-71-2; CHF₂PCL₂, 97523-72-3; (CHF₂)₂P-P(CF₃)₂, 97523-73-4; P₂(CF₃)₄, 2714-60-5; (CF₃)₂PH, 460-96-8; (C-F₃)₂PCL, 650-52-2; (CHF₂)₂PH·BH₃, 97551-00-3; B₂H₆, 19287-45-7; (CHF₂)₃P·BH₃, 97523-75-6; P₂(CHF₂)₄·BH₃, 97523-76-7; (CHF₂)₃PO, 97523-74-5; (CF₃)₃P, 432-04-2; (CF₃)₃PO, 423-01-8; (CHF₂CO)₂O, 401-67-2; CHF₂OC(O)CHF₂, 2002-63-3; AgCO₂CHF₂, 383-88-0; Hg₂(CO₂CHF₂)₂, 97523-77-8.

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Ammoniation Reactions of *cis*- and *trans*-[Co(en)₂XY]ⁿ⁺ Complexes in Liquid Ammonia, Related to the Bailar Inversion Reaction

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Base-catalyzed ammoniation is described for a number of complexes from the series *cis/trans*-[Co(en)₂XY]ⁿ⁺ (X, Y = Cl⁻, Br⁻, Me₂SO, DMF), where both X and Y are readily substituted ligands. Some members of the series with *trans* configuration have rate-limiting deprotonation (X, Y = Cl⁻, Cl⁻; Br⁻, Br⁻; Cl⁻, Me₂SO). ¹H NMR spectra of the products, directly recorded in the reaction medium, established, besides the normal two-step ammoniation reaction, the presence of an additional pathway involving the simultaneous loss of both ligands X and Y. The percentage of double substitution varies from 23% (X, Y = Cl⁻, DMF) to 65% (Br⁻, Br⁻). The [Co(en)₂(NH₃)₂]³⁺ formed is a mixture of *cis* and *trans* isomers. The percentage of double substitution seems to depend primarily on the nature of the most strongly bound of the ligands X and Y, whereas the percentage of the *trans* complex in the diammine depends on the weakest bound ligand. The product distribution is independent of pH and temperature. For the Δ-(+)-[Co(en)₂Br₂]⁺ ion, the double substitution leads to a net inversion for the *cis*-diammine reaction product. By the use of deuterated ammonia as reaction medium, information was collected on the fate of specific proton sites during the reaction. Arguments are presented that the double-ligand-loss pathway originates in an attack of a solvent molecule on the five-coordinate intermediate of the traditional dissociative conjugate-base mechanism.

Introduction

Recently a reinvestigation of the Bailar inversion reaction¹ by Jackson and Begbie² has established a unique base-catalyzed route, by which Δ-[Co(en)₂Cl₂]⁺ (en = ethylenediamine) hydrolyzes with the simultaneous loss of both Cl⁻ ligands. These authors suggested² that both *cis*- and *trans*-[Co(en)₂XY]ⁿ⁺ complexes with two readily substituted ligands X and Y could behave similarly to Δ-[Co(en)₂Cl₂]⁺. To us, it seemed that some of the missing information on these systems, required to formulate a detailed reaction pathway, could be obtained from liquid-ammonia studies. The reason is that some of the systems expected to exhibit double substitution also are in the category for rate-limiting deprotonation³ in liquid ammonia.⁴ This makes it possible to establish the number and position of deprotonations leading to the reactive intermediate(s). In addition, systems showing the normal mechanism of base-catalyzed ammoniation often have widely differing rates of

¹H-²H exchange at either side of the Co(en)₂ plane, which opens up the possibility to use ¹H labels in liquid N²H₃ to follow the steric course.⁵ Finally, the product distribution can be determined directly in liquid ammonia by ¹H NMR.⁶

We present here a study of the ammoniation of a number of *cis*- and *trans*-[Co(en)₂XY]ⁿ⁺ complexes, with X, Y = Br⁻, Cl⁻, Me₂SO (dimethyl sulfoxide), DMF (dimethylformamide), which have as one of the reaction pathways a route involving the concerted loss of both X and Y.

Experimental Section

Materials. *cis*- and *trans*-[Co(en)₂(Me₂SO)Cl](ClO₄)₂,⁷ *cis*-[Co(en)₂(Me₂SO)₂](ClO₄)₃,⁸ Δ-(+)-[Co(en)₂Cl₂](ClO₄) and Δ-(+)-[Co(en)₂Br₂](ClO₄)₂,⁸ and *trans*-[Co(en)₂BrCl](ClO₄)₂⁹ were prepared according to published methods. The identity and isomeric purity of the complexes followed from UV-visible, ORD, and ¹H NMR spectra. Analysis results were satisfactory. The *cis* and *trans* isomers of the compounds [Co(en)₂Cl₂](ClO₄), [Co(en)₂Br₂](ClO₄), [Co(en)₂(NH₃)Cl](ClO₄)₂, and [Co(en)₂(NH₃)Br](ClO₄)₂ were used from previous

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