[CONTRIBUTION FROM RESEARCH & ENGINEERING DIVISION, MONSANTO CHEMICAL CO.]

π-Complexes of the Transition Metals. VIII. The Preparation and Reactions of Triphenylchromium(III)[1]

BY W. HERWIG AND H. ZEISS

RECEIVED NOVEMBER 13, 1958

The preparation of the first member of a series of σ-bonded organochromium compounds, triphenylchromium(III), is reported in detail. The rearrangements which this red, crystalline substance undergoes to yield bis-arene chromium π-complexes are described and then explained in terms of an internal oxidation–reduction process.

The reaction of phenylmagnesium bromide with chromic trichloride in diethyl ether to give bis-arene chromium π-complexes has been described and broadly discussed in several earlier publications.[1b,2] By changing the solvent medium from ether to tetrahydrofuran, the key relay intermediate in this reaction has been intercepted and isolated. This intermediate has been proved to be triphenylchromium(III)[3] in the form of its tetrahydrofuranate. The experimental conditions for obtaining this substance and its role as intermediate in the formation of the π-complexes, or bis-arene chromium "sandwiches," are reported in this paper.

In a series of experiments designed to elucidate the course of reaction between metallic halides and Grignard reagents, chromic trichloride and phenylmagnesium bromide were allowed to react in different molar ratios and in several solvents. In diethyl ether, so long as the amount of Grignard reagent was maintained in excess of 3:1 over the metal halide, no effect of a change of their relative concentrations was observed either on the total yield (25–35%) or on the usual 1:1 ratio of the π-complexed products, bis-benzene-chromium and benzene-biphenyl-chromium. However, a slight increase in yield (from trace amounts to 3%) of bis-biphenyl-chromium was detected when a large excess (8:1) of phenylmagnesium bromide and a long reaction period (36 hours) were employed. The same product ratio and yield were obtained also when the reaction was carried out in diethyl ether containing added biphenyl.[4] Consequently, *free* biphenyl, arising as a by-product during the preparation of phenylmagnesium bromide, is not a factor affecting the course of this reaction. Substantially the same results were obtained in tetrahydrofuran as solvent except that precipitation of the black, pyrophoric solid intermediate[12] was not observed. However, when an *exact* mole ratio of 3:1 ($C_6H_5MgBr/CrCl_3$) was used in the latter solvent, a strikingly different experimental result was obtained. The reacting solution, in which the insoluble, violet, anhydrous chromic trichloride dissolves with subsequent precipitation of a black solid and development of dark color when diethyl ether is used, instead became a red-brown colored mixture as the solid halide disappeared and then deposited the bright red, crystalline triphenylchromium(III) tetrahydrofuranate. Hydrolysis of either this precipitate or its mother liquor produced green chromium(III) ion, but not a trace of π-complex cation. However, after a tetrahydrofuran solution of this solid had stood for about 8 hours in the presence of phenylmagnesium bromide, π-complex cation was detectable by tetraphenylboron ion precipitation. Also, if a tetrahydrofuran solution of the solid was poured into ether, π-complex again was formed. These results showed clearly that the π-complex formation step had been isolated from the over-all reaction sequence.

The structural proof of triphenylchromium(III) as $(C_6H_5)_3Cr(III)$ rests upon both physical and chemical evidence. The substance exhibits a paramagnetic susceptibility of 3.89 Bohr magnetons which compares closely with the 3.86 value for Cr(III) halides. A plot of the variation of the reciprocal of its magnetic susceptibility with absolute temperature (Fig. 1) describes a straight line passing through the origin as required for a pure substance behaving normally.[5] Triphenylchromium(III) in tetrahydrofuran solution is cleaved quantitatively by mercuric chloride and yields precisely 3 moles of phenylmercuric chloride for each mole of triphenylchromium(III) in the solution. At the same time chromium(III) trichloride tetrahydrofuranate is formed and may be crystallized from the solution as the violet $CrCl_3 \cdot 3$ THF.[6]

Additional evidence for the composition of the solvated complex of triphenylchromium(III) is found in the quantitative loss of tetrahydrofuran from its crystalline tetrahydrofuranate form corresponding to a mole of triphenylchromium coördinated with exactly 3 moles of tetrahydrofuran: $(C_6H_5)_3Cr \cdot 3THF$. The significance of this result is enhanced by the observation that the removal of the coördinating solvent molecules causes the concurrent conversion of triphenylchromium(III) into a black, pyrophoric solid resembling that found in the diethyl ether experiments. This color change is a consequence of a profound structural change, for it is not possible to regenerate triphenylchromium by dissolving the black material in tetrahydrofuran. This latter solution reduces mercuric chloride and does not yield phenylmercuric chloride. Hydrolysis of this solution in the presence of air produces an aqueous solution of the π-complexes, bis-benzene-chromium(I) and benzene-biphenyl-chromium(I), *in the same ratio and in almost the*

---

(1) (a) Preliminarily communicated to THIS JOURNAL, **79**, 6561 (1957); (b) paper VII, M. Tsutsui and H. Zeiss, *ibid.*, **81**, 1367 (1959).

(2) H. Zeiss and M. Tsutsui, *ibid.*, **79**, 3062 (1957).

(3) F. Hein and R. Weiss, *Z. anorg. Chem.*, **295**, 145 (1958), have more recently reported the isolation of this substance in the form of its addition compound with phenyllithium and diethyl ether.

(4) These results were obtained by Dr. M. Tsutsui of our laboratory.

(5) We sincerely appreciate the assistance and interest of Dr. R. B. Johannesen of the National Bureau of Standards, Washington, D. C., in the measurement and interpretation of these magnetic susceptibilities.

(6) W. Herwig and H. Zeiss, *J. Org. Chem.*, **23**, 1404 (1958).

same total yield (20–25%) as are obtained from reactions between phenylmagnesium bromide and chromic trichloride from which intermediates are not isolated. We conclude, therefore, that rearrangement of the σ-bonded triphenylchromium(III)[7] to the π-bonded chromium complexes occurs when its coördinating molecules of tetrahydrofuran are lost either by the washing action of diethyl ether, by removal with reduced pressure or by the effect of temperatures above the boiling point of tetrahydrofuran at atmospheric pressure. As a corollary to this conclusion it is believed that triphenylchromium is incapable of existence unless stabilized by molecules, such as of tetrahydrofuran, which are sufficiently basic to effectively coördinate trivalent chromium. Diethyl ether, on the other hand, is not basic enough to stabilize triphenylchromium, and so the reaction of chromic trichloride and phenylmagnesium bromide in this solvent proceeds to π-complex formation without interruption.

The black material obtained by the collapse of triphenylchromium(III) is also strongly paramagnetic but becomes less so with passage of time. It is found that its magnetic susceptibility is a peculiar function of temperature and does not increase rapidly enough with decreasing temperature to satisfy the law, $\chi(T - \Delta) = \text{constant}$ (Fig. 1).[5] This anomalous behavior is consistent with our conclusion that the black material is a mixture, since on hydrolysis *under nitrogen* it yields a 1:1 mixture of bis-benzene-chromium(0) and benzene-biphenyl-chromium(0) in a total yield of 20–25%. This hydrolysis step is clearly required in order to isolate the π-complexes, since attempts to sublime either or both of the zerovalent complexes from the black material *prior* to hydrolysis results in the thermal destruction of the π-complexed intermediates and a copious yield of biphenyl.

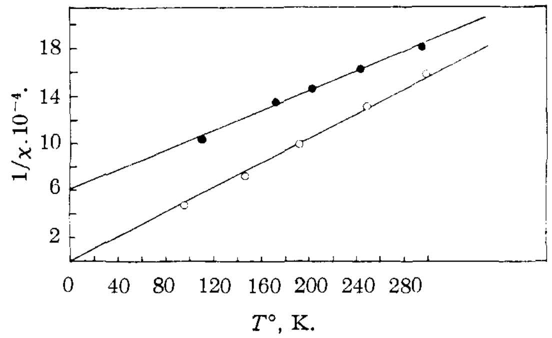
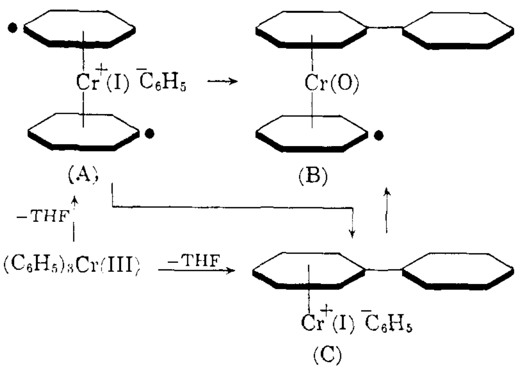
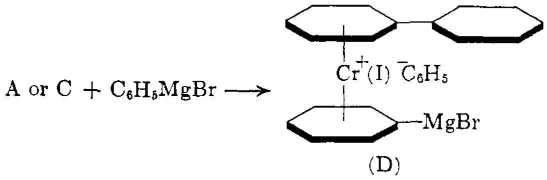


Fig. 1.—1/Magnetic susceptibility per gram (χ) *vs.* temperature for triphenylchromium(III)-magnesium halide, ○, and black solid, ●.

The reduction of chrom*ous* chloride with phenylmagnesium bromide has been interpreted on the basis of data similar to that just described as proceeding *via* the formation of diphenylchromium(II) and subsequent internal rearrangement to the π-complexed chromium(0) intermediates which liberate the final products, bis benzene-chromium(0) and benzene-biphenyl-chromium(0) on hydrolysis.[1b] Extension of this hypothesis to the rearrangement of triphenylchromium(III) to π-complexed intermediates presents, however, at least one important difference in that the reduction of chromium can proceed by this type of rearrangement only to the monovalent level. Therefore, a second reduction step is required in order to obtain the completely reduced chromium(0) complexes. The rearrangement scheme tentatively proposed here is supported by the following considerations. The mixture of intermediates (black material) represented in the reaction diagram as A, B and C, resulting from the loss of tetrahydrofuran from the solvated triphenylchromium(III), is paramagnetic and very sensitive to both air and water. Solvolysis of this mixture with deuterium oxide leads to the incorporation of one deuterium atom into each phenyl radical but none into biphenyl.[8] Thermal decomposition of the mixture produces free biphenyl and causes complete loss of π-complex character. The hydrolytic process, however, remains an enigma, and the final reduction of chromium to the zero-valent state is presently not understood.



Another significant piece of evidence supporting this rearrangement scheme is the behavior of triphenylchromium(III) with *phenylmagnesium bromide* in tetrahydrofuran. If these reagents are refluxed together for several hours and then hydrolyzed, the sole product is benzene-biphenyl-chromium(I) *cation*. This result is interpreted as the outcome of the thermal rearrangement of triphenylchromium(III) *in solution* to A and/or C, followed by the addition of Grignard reagent to form D. Hydrolysis of this latter intermediate leads to the cation and not to the chromium(0)



---

[7] Our assumption of σ-bonding rather than ionic bonding of phenyl-to-chromium(III) is based on the experimental fact of the failure of trimesitylchromium(III), as well as dimesitylchromium(II) [*cf.* ref. 1b], to undergo rearrangement to π-complex, indicating that an important steric factor arising from close bonding between carbon and chromium is involved. Furthermore, a formulation of phenide ion bonding to chromium is not consistent with the rearrangements which are required to account for the properties and behavior of the intermediate products (*vide infra*).

[8] H. Zeiss and W. Herwig, *Ann.*, **606**, 209 (1957).

complexes.[9] On the other hand, if triphenylchromium(III) is first rearranged in its solid state to the black material, then treated with phenylmagnesium bromide and hydrolyzed, the ratio of bis-benzene-chromium to benzene-biphenyl-chromium is changed from the usual 1:1 to 1:4, indicating that A is being consumed by Grignard reagent. The working concepts discussed here are being applied in the general area of reactions between metallic halides and Grignard reagents.

Experimental[10]

Preparation of Triphenylchromium(III) Tetrahydrofuranate. (a) With Chromium Trichloride Tetrahydrofuranate.—Anhydrous chromium trichloride (12.21 g., 77.2 mmoles) was extracted quantitatively into 140 ml. of tetrahydrofuran as described in a previous publication.[6] This mixture of dissolved and suspended tetrahydrofuranate now was diluted with 310 ml. of tetrahydrofuran and then cooled in a three-necked flask under nitrogen to −30°. To this solution was added 220 ml. (235 mmoles) of phenylmagnesium bromide (1.07 *M* in THF) over a period of 45 minutes with vigorous stirring. The violet color of the solution changed immediately to red-brown, accompanied by the precipitation of a dark red solid. After dilution with 200 ml. of tetrahydrofuran the mixture was stirred for 4 hours at room temperature under nitrogen. The result is a completely clear, dark red-brown solution of triphenylchromium(III) tetrahydrofuranate (approximately 900 ml. of a 0.25 *N* solution). However, if the reaction mixture is finally diluted to a total volume of 750 ml. with tetrahydrofuran and then stirred, 1.2 g. of blood-red needles of triphenylchromium(III) tritetrahydrofuranate, m.p. 85° dec., can be isolated by filtration under nitrogen. The solubilities of this compound and magnesium halide in tetrahydrofuran are so close that separation by fractional crystallization from that solvent is achieved with only limited success.

Anal. Calcd. for $(C_6H_5)_3Cr\cdot 3THF$: Cr, 10.4; THF, 41.5; halide, 0. Found: Cr, 10.2; THF, 43.4; halide, 0.18.

Alternatively, solid triphenylchromium tritetrahydrofuranate completely free of magnesium halide salt could be isolated in small yields by fractional precipitation from a dilute solution of its mixed salt in tetrahydrofuran with addition of an equal volume of diethyl ether. This red, crystalline precipitate was cleaved quantitatively with mercuric chloride in tetrahydrofuran to pure phenylmercuric chloride, m.p. 266–267°.

Anal. Calcd. for $(C_6H_5)_3Cr\cdot 3THF$: Cr, 10.4; Cr/C_6H_5, 1:3; C_6H_5, 46.2. Found: Cr, 9.8; Cr/C_6H_5, 1:2.8; C_6H_5, 40.2.

(b) With Chromium Trichloride.—A solution of phenylmagnesium bromide in tetrahydrofuran (142.5 ml., 0.61 *M*, 87 mmoles) was magnetically stirred under nitrogen in a Schlenk tube at −25° while 4.5 g. (28.5 mmoles) of anhydrous, solid chromium trichloride was added in one portion. Reaction commenced immediately at the surface of the metal halide with development of a greenish-brown color in the solution phase. After 8 hours under the same conditions, the reaction mixture consisted of a heavy, red, homogeneous salt, a red-brown supernatant mother liquor and a few violet flakes of unreacted chromium trichloride. The mixture was next filtered at 10° in an atmosphere of nitrogen, and the red salt on the filter was washed 4 times with 20-ml. portions of cold (10°) tetrahydrofuran.[11] The solid then was dried at room temperature under nitrogen at 20 mm. for 3 hours: 23.3 g. (72%). The mother liquor yielded a second fraction at −10° and on limited dilution with ether yet a third fraction of this salt. These salts can be recrystallized from tetrahydrofuran at 50°.

Anal. Calcd. for $(C_6H_5)_3Cr\cdot 3MgBrCl\cdot 6THF$: Cr, 4.58; THF, 38.1. Found: Cr, 4.62, 4.78; THF, 37.0, 39.3.

A sample (2.29 g., 2.02 mmoles) of the recrystallized triphenylchromium-magnesium halide salt was cleaved quantitatively with mercuric chloride in tetrahydrofuran to 1.94 g. (6.19 mmoles) of the insoluble, pure phenylmercuric chloride, m.p. 266–267°. Titration of the chromium(III) ion remaining in solution gave a chromium determination of 0.105 g. (2.02 mmoles).

Anal. Calcd. for $(C_6H_5)_3Cr\cdot 3MgBrCl\cdot 6THF$: Cr, 4.58; Cr/C_6H_5, 1:3; C_6H_5, 20.4. Found: Cr, 4.58 (*sic*); Cr/C_6H_5, $1:3.0_6$; C_6H_5, 20.8.

Rearrangement of Triphenylchromium(III). (a) Under Reduced Pressure.—The red triphenylchromium(III), either in the form of its pure tetrahydrofuranate or combined with magnesium halide, can be rearranged completely to a black solid (admixed with white magnesium salt in the latter case) between 20–40° and at 0.05 mm. over a period of 2–4 hours. This black material is pyrophoric, soluble in tetrahydrofuran, insoluble in diethyl ether, and, when hydrolyzed with oxygen-free water under nitrogen, may be extracted quantitatively into benzene as bis-arene chromium(0) complexes. These complexes may then be transferred quantitatively into an aqueous layer in the presence of air as the chromium(I) cations and then precipitated with sodium tetraphenylboron for yield determination, identification (infrared), and recrystallization. Since the loss of tetrahydrofuran from either coördination compound of triphenylchromium(III) is quantitative, the total yield data which follow are based on chromium. Thus, 1.70 g., 4.78 g. and 4.79 g. of black solid gave after hydrolysis 0.26 g. (19%), 0.85 g. (22%) and 0.90 g. (23%) of mixed tetraphenylboron salt, respectively. These salts contained bis-benzene-chromium(I) and benzene-biphenyl-chromium(I) in percentage ratios of 43:57, 56:44 and 60:40, respectively. The benzene-biphenyl-chromium fraction always contained traces of bis-biphenyl-chromium salt.

(b) With Diethyl Ether.—The addition of either solid triphenylchromium(III) tritetrahydrofuranate or its magnesium halide salt to ether immediately produced rearrangement and formation of a black powder. This powder had the exact properties of the material described in the preceding section. For example, 4.44-g. and 2.78-g. samples of the triphenylchromium-magnesium halide salt gave after ether rearrangement, hydrolysis and tetraphenylboron ion precipitation 0.48 g. (22%) and 0.32 g. (23%) of mixed tetraphenylboron salts of the chromium complexes. Product ratios were nearly the same as those found in the preceding section, being about 50:50 in both cases.

(c) By Heating.—A sample of triphenylchromium(III) tritetrahydrofuranate was warmed in a narrow tube under nitrogen and at atmospheric pressure. At 85° the sample decomposed with foaming to a black solid which on hydrolysis in air dissolved to give a yellow solution. The addition of sodium tetraphenylboron to this solution caused the precipitation of bis-arene chromium complexes as described in the preceding sections.

(d) In the Presence of Phenylmagnesium Bromide.—A 2.3-g. sample of triphenylchromium-magnesium halide salt was treated with 18 ml. (17 mmoles) of phenylmagnesium bromide in tetrahydrofuran, allowed to stand for 1.5 hours and then refluxed for 1 hour. The brown-black solution now was hydrolyzed under nitrogen in the presence of benzene to give a yellow-green aqueous layer and a yellow-brown benzene layer. Tetraphenylboron ion precipitation of the aqueous layer gave 0.2 g. (17%) of benzene-biphenyl-chromium(I) salt, but the benzene layer failed to yield any water-soluble cation in the presence of air and consequently any trace of chromium complex.

---

(9) This experiment was performed the first time in a very qualitative fashion and gave as sole product unquestionably pure bis-biphenyl-chromium. However, subsequently and consistently, this reaction always produced benzene-biphenyl-chromium cation when repeated carefully both by us and by Dr. W. Metlesics of our laboratory on several different occasions. The former singular result may be explained as a quantitative conversion of A and/or C into the intermediate B, and the reaction of B with phenylmagnesium bromide to give bis-biphenyl-chromium. However, the experimental conditions for producing this total conversion have not been duplicated.

The mesityl radical has been introduced successfully into the π-complexed cation by Dr. Metlesics who rearranged triphenylchromium(III) in tetrahydrofuran in the presence of mesitylmagnesium bromide. The incorporation of a mesityl group into the complex is clearly evident from the appearance of mesityl absorption characteristics in the infrared spectrum of the tetraphenylboron salt of the complex and is also consistent with the rearrangement of triphenylchromium to π-complexed intermediates, such as those produced above.

(10) G. E. lamp-grade nitrogen was used in all experiments.

(11) A considerable amount of salt was lost from the filter during this washing.

The anomalous experiment referred to in reference 9 involved the reaction of triphenylchromium with a 6-fold excess of phenylmagnesium bromide in tetrahydrofuran for 2 hours. After hydrolysis of the dark solution, the sole product isolated was the bis-biphenyl-chromium(I) cation in 16% yield.

Reaction of Black Solid with Phenylmagnesium Bromide.—A 10.4-g. sample of triphenylchromium-magnesium halide salt was rearranged to black solid at 50° (0.05 mm.). This material then was dissolved in 70 ml. of a 1.1 *M* solution of phenylmagnesium bromide in THF and refluxed for 2 hours. After hydrolysis of the reaction solution according to the previously described procedure, 0.61 g. (12%) of a mixed tetraphenylboron salt was precipitated which consisted of a 20:80 mixture of bis-benzenechromium(I) and benzene-biphenylchromium(I) salts.

DAYTON 7, OHIO

[CONTRIBUTION NO. 528 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Addition of Phosphines to Fluoroölefins

BY G. W. PARSHALL, D. C. ENGLAND AND R. V. LINDSEY, JR.

RECEIVED FEBRUARY 11, 1959

Phosphine and phenylphosphine undergo thermal addition to fluoroölefins to give fluoroalkylphosphines. Reaction of phosphine with tetrafluoroethylene gave the mono- and bis-(1,1,2,2-tetrafluoroethyl)-phosphines and, unexpectedly, tetrafluoroethylenediphosphine. Similar products were obtained with phosphine and chlorotrifluoroethylene and dichlorodifluoroethylene, but only monoaddition products resulted from reaction with 1,1-difluoroethylene, 1,1-difluoroisobutylene and hexafluoropropene.

Silanes have been reported to add to fluoroolefins in the presence of free-radical catalysts and the extension of this type of reaction to other metalloid hydrides has been considered.[1] Tin hydrides have since been added to tetrafluoroethylene[2] and free-radical-,[3] acid-[4] and base-[5] catalyzed additions of phosphine to non-fluorinated olefins have been reported.

Phosphine has now been found to react with fluoroölefins in the absence of a catalyst to give fluoroalkylphosphines. Phosphine and tetrafluoroethylene, for example, react at 150° in a sealed glass tube to give 1,1,2,2-tetrafluoroethylphosphine (I), bis-(1,1,2,2-tetrafluoroethyl)-phosphine (II) and, surprisingly, tetrafluoroethylenediphosphine (III). Octafluorocyclobutane and

$HCF_2CF_2PH_2$ I $(HCF_2CF_2)_2PH$ II $H_2PCF_2CF_2PH_2$ III

1,1,2,2-tetrafluoroethane were also detected among the gaseous products. A similar range of products was obtained by the addition of phosphine to chlorotrifluoroethylene and to dichlorodifluoroethylene as shown in Table I. The reaction of phosphine with 1,1-difluoroethylene, 1,1-difluoroisobutylene and hexafluoropropene gave only the monoaddition products.

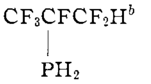
The reaction of phenylphosphine with tetrafluoroethylene gave phenyl-1,1,2,2-tetrafluoroethylphosphine (IV) in 45% yield and a trace of bis-(1,1,2,2-tetrafluoroethyl)-phenylphosphine (V).

$C_6H_5PHCF_2CF_2H$ IV $C_6H_5P(CF_2CF_2H)_2$ V

The fluoroalkylphosphines obtained in these reactions are clear, colorless, spontaneously flammable liquids. These compounds are much less basic than the corresponding alkylphosphines and undergo conventional phosphine reactions, such as quaternization, slowly, if at all.

TABLE I

PRODUCTS OF THE ADDITION OF PHOSPHINE TO FLUOROÖLEFINS

Olefin	Product	B.p., °C.	Yield[c]
$CF_2{=}CF_2$	$HCF_2CF_2PH_2$	20–22	53
	$(HCF_2CF_2)_2PH$	91–92	7
	$H_2PCF_2CF_2PH_2$	69–72	9
	HCF_2CF_2H	....	[a]
	C_4F_8	....	[a]
$CFCl{=}CF_2$	$HCFClCF_2PH_2$	67	54
	$(HCFClCF_2)_2PH$	138–142	6
	$H_2PCFClCF_2PH_2$	107–109	1
	$HCFClCF_2H$	20	[a]
$CCl_2{=}CF_2$	$HCCl_2CF_2PH_2$	109.5–110.5	30
	$(HCCl_2CF_2)_2PH$	180–184	3
	$H_2PCCl_2CF_2PH_2$	*ca.* 140	[a]
	$HCCl_2CF_2H$	45–47	[a]
$CH_2{=}CF_2$	$HCF_2CH_2PH_2$[b]	52–53.5	1
$(CH_3)_2C{=}CF_2$	$(CH_3)_2CHCF_2PH_2$[b]	75–77	6
$CF_3CF{=}CF_2$	 $\underset{PH_2}{CF_3\overset{\vert}{C}FCF_2H}$[b]	45–48	36

[a] Product not isolated in pure form; characterized only by infrared or nuclear magnetic resonance analysis. [b] Structure tentatively assigned by nuclear magnetic resonance analysis. [c] Per cent. based on the amount of phosphine charged.

The products obtained from 1,1-difluoroethylene and from 1,1-difluoroisobutylene were characterized only by their mass spectra and H^1 and F^{19} magnetic resonance spectra. The choice of isomers of these products was made on the basis of the presence or absence of CF_2H groups in the H^1 and F^{19} magnetic resonance and mass spectra.

Experimental[6]

General Procedure.—All the phosphine addition reactions were carried out in sealed glass tubes which were heated at 150° for 8 hours. Equimolar quantities of phosphine and fluoroölefin were used and the products were isolated by distillation of the reaction mixture as described in the phosphine–tetrafluoroethylene reaction below. The products

---

[1] A. M. Geyer and R. N. Haszeldine, *Nature*, **178**, 808 (1956).

[2] C. G. Krespan and V. A. Engelhardt, *J. Org. Chem.*, **23**, 1565 (1958).

[3] A. R. Stiles, F. F. Rust and W. E. Vaughan, THIS JOURNAL, **74**, 3282 (1952).

[4] H. C. Brown, U. S. Patent 2,584,112, Feb. 5, 1952.

[5] I. Hechenbleickner and M. M. Rauhut, U. S. Patent 2,822,376, Feb. 4, 1958.

[6] Melting and boiling points are uncorrected.