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POLYFLUOROALLYL AND PROPENYL DERIVATIVES OF SOME TRANSITION AND GROUP V ELEMENTS

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SUMMARY

The compound (2-chlorotetrafluoroallyl)manganese pentacarbonyl has been prepared, and its facile rearrangement to a propenyl isomer has been studied. The stereochemical results of the rearrangement are compared with those of cesium fluoride induced rearrangements of some analogous (polyfluoroallyl)arsenic and -phosphorus compounds. It is suggested that the rearrangement of the manganese compound is a consequence of the weakening of the α-C–F bond, and the resulting presence of an internal nucleophile in the compound. Infrared and NMR spectral data for the compounds investigated are collected and discussed.

INTRODUCTION

There is a great deal of current interest in polyfluoroalkyl derivatives of the transition elements[1,2] and one feature of these compounds which has attracted attention is the nature of the carbon–metal bond. Recent X-ray diffraction studies, for example[3], have shown that the carbon–molybdenum bond length in π-$C_5H_5Mo(CO)_3C_3F_7$ is significantly shorter than that in an analogous unfluorinated complex, π-$C_5H_5Mo(CO)_3C_2H_5$. There is also evidence from infrared spectroscopy[4] and nuclear magnetic resonance spectroscopy[5,6] that fluorine atoms are rather weakly bound to the carbon atom attached to the metal.

A chemical observation which is interesting in this connection is that in the reaction between perfluoroallyl chloride and manganese pentacarbonyl anion, the isolated product is (perfluoropropenyl)manganese pentacarbonyl, rather than the expected (perfluoroallyl)manganese pentacarbonyl[7], though there was some indication that the allyl compound was first formed and isomerized spontaneously[8].

$$CF_2{=}CF{-}CClF_2 + Mn(CO)_5^- \rightarrow [CF_2{=}CF{-}CF_2Mn(CO)_5] \rightarrow CF_3{-}CF{=}CFMn(CO)_5$$

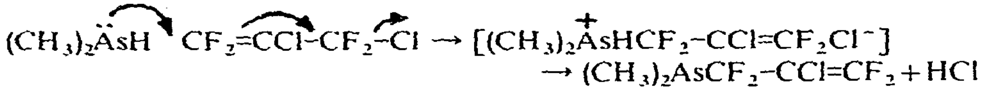
This suggests that a facile shift of the α-fluorine atom in such a polyfluoroallyl derivative of a transition metal may be possible. This present investigation has been concerned with the preparation of such a polyfluoroallyl compound, a study of its rearrangement to a propenyl derivative, and a comparison of this rearrangement with those of some analogous compounds of arsenic and phosphorus.

RESULTS AND DISCUSSION

Preparation of polyfluoroallyl compounds

The compounds studied were prepared by the attack of a suitable nucleophile on 2,3-dichlorotetrafluoropropene. A straightforward synthesis of this olefin, and its high degree of reactivity towards nucleophiles containing phosphorus, have been described recently[9].

Reaction between 2,3-dichlorotetrafluoropropene and dimethylarsine proceeded slowly at room temperature to give a high yield of (2-chlorotetrafluoroallyl)dimethylarsine; this reaction is presumed to occur via nucleophilic attack of the arsine on the olefin, by analogy with comparable reactions with phosphines[9].



$$(CH_3)_2\ddot{A}sH\ \ CF_2{=}CCl{-}CF_2{-}Cl \rightarrow [(CH_3)_2\overset{+}{A}sHCF_2{-}CCl{=}CF_2Cl^-]$$
$$\rightarrow (CH_3)_2AsCF_2{-}CCl{=}CF_2+HCl$$

The reaction rate for dimethylarsine was slower than that for dimethylphosphine, indicative of the lower nucleophilicity of the arsine. Characterization of (2-chlorotetrafluoroallyl)dimethylarsine, as well as other new compounds reported, was by elemental analysis, infrared spectroscopy (see Table 1) and ^1H (see Table 2) and ^{19}F (see Table 3) nuclear magnetic resonance (NMR) spectroscopy.

Reaction between 2,3-dichlorotetrafluoropropene and manganese pentacarbonyl anion in dilute tetrahydrofuran solution was rapid. A mild work-up proce-

TABLE 1

IR SPECTRA OF $CF_2{=}CCl{-}CF_2G$ COMPOUNDS (cm^{-1})

G	$\nu(C{=}C)$	$\nu(F{-}C{=}C)$	$\nu(F{-}CG)$	$\nu(C{-}H)$	$\nu(CO)$
$As(CH_3)_2$[a]	1737	1323	1030	2930, 2995	
$Mn(CO)_5$[b]	1727	1308	980		2015, 2032 2068, 2125

[a] Gas phase. [b] Solution in $CHCl_3$.

TABLE 2

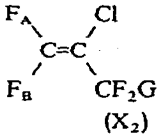
^1H NMR SPECTRA

Compound	Chemical shifts, δ (ppm)[a]	Coupling constant J (Hz)
$CF_2{=}CCl{-}CF_2As(CH_3)_2$	CH_3, 1.15 (singlet)	
$CF_3{-}CCl{=}CFAs(CH_3)_2$	CH_3, 1.27 (doublet, both *cis* and *trans*)	J(HCAsCF) 0.9
$(\pi\text{-}C_5H_5)Fe(CO)_2CF{=}CClCF_3$	C_5H_5, 5.04 (singlet)	
$CF_3{-}CCl{=}CFP(C_6H_5)_2$	C_6H_5, 7.0–7.2 (complex multiplet)	
cis-$CF_3{-}CCl{=}CFP(O)(OCH_3)_2$	CH_3, 4.27 (doublet of doublets)	J(HCOP) 14.0 J(HCOPCF) 0.45
trans-$CF_3{-}CCl{=}CFP(O)(OCH_3)_2$	CH_3, 4.32 (doublet of doublets)	J(HCOP) 13.6 J(HCOPCF) 0.40

[a] Downfield from internal $(CH_3)_4Si$.

TABLE 3

^{19}F NMR SPECTRA OF



$(F_A)(F_B)C{=}C(Cl)CF_2G\ (X_2)$

G	Chemical shifts, δ (ppm)[a]			J (Hz)		
	A	B	X	AX	BX	AB
$As(CH_3)_2$	79.9	80.8	100.4	8.0	26.8	24.6
$Mn(CO)_5$	89.0	84.2	44.9	6.5	32.1	35.8

[a] Upfield from internal $CFCl_3$.

dure, in which the resulting materials were not heated above 40°, yielded colorless, volatile crystals of (2-chlorotetrafluoroallyl)manganese pentacarbonyl:

$$CF_2{=}CCl{-}CClF_2+Mn(CO)_5^- \rightarrow CF_2{=}CCl{-}CF_2Mn(CO)_5+Cl^-$$

Infrared spectra of polyfluoroallyl compounds

A previous study of compounds of this type[9] has shown characteristic intense bands in the region of 1715–1740 cm^{-1}, associated with the double bond stretching frequency, 1310–1340 cm^{-1}, associated with a vibration of a fluorine attached to a doubly bonded carbon atom, and 1015–1050 cm^{-1}, associated with a fluorine attached to a four-coordinate carbon atom. These characteristic bands are all present in the infrared spectrum of (2-chlorotetrafluoroallyl)dimethylarsine (Table 1). However, the spectrum of (2-chlorotetrafluoroallyl)manganese pentacarbonyl is anomalous; while there are intense bands at 1727 cm^{-1} and 1308 cm^{-1}, representative of the first two classes of vibration mentioned, there is no intense band in the 1015–1050 cm^{-1} region. Instead, an intense band appears at 980 cm^{-1} in a spectral region which is blank in the other compounds studied. It is suggested that this band is associated with a carbon–fluorine stretching vibration of the CF_2Mn group, and that the pronounced lowering of frequency is attributable to a weakening of this C–F bond. This is parallel to earlier observations[4] on the C–F stretching frequencies in CF_3-$Mn(CO)_5$, which are significantly lower than those in, say, CF_3Cl.

NMR spectra of polyfluoroallyl compounds

The ^{19}F NMR spectra of the polyfluoroallyl compounds are of the ABX_2 type (see Table 3) and can be analysed by first-order methods. The chemical shifts of the AB fluorine nuclei, those attached directly to unsaturated carbon in the manganese derivative are at rather higher field than those of similarly situated nuclei in other polyfluoroallyl compounds[9]. The chemical shift of the X_2 fluorine nuclei in the manganese compound are at low field compared to corresponding nuclei in the arsenic compound or in a variety of phosphorus derivatives. This deshielding effect has been often observed in CF_2 groups and CF_3 groups bonded to transition metals[10], and has been attributed to mixing of low-lying excited states involving interaction between filled *p*-orbitals on fluorine and vacant *d*-orbitals on the metal[5]. However, the chemical shift of CF_2 groups in 2-chlorotetrafluoroallyl compounds varies over a wide range, even in compounds where the group is bonded to a main group element (see Table 4). The present theoretical basis of ^{19}F chemical shifts does not seem adequate to explain observations of this type, and it seems premature to advance explanations involving special effects for transition metal compounds on the basis of the limited data available.

Production of polyfluoropropenyl compounds

The rearrangements of four allylic compounds to their propenyl isomers were studied, *viz.* those of (2-chlorotetrafluoroallyl)diphenylphosphine [CF_2=CCl–$CF_2P(C_6H_5)_2$], dimethyl (2-chlorotetrafluoroallyl)phosphonate [CF_2=CCl–$CF_2P(O)(OCH_3)_2$], (2-chlorotetrafluoroallyl)dimethylarsine [CF_2=CCl–$CF_2As(CH_3)_2$] and (2-chlorotetrafluoroallyl)manganese pentacarbonyl [CF_2=CCl–$CF_2Mn(CO)_5$]. The phosphorus and arsenic compounds do not rearrange spontaneously on being heated nor do they rearrange rapidly on being treated with a solution of tetraethylammonium fluoride in chloroform[11]. They were rearranged in high yield to 2-chlorotetrafluoropropenyl compounds when they were heated with cesium fluoride.

In contrast to this, a multiply sublimed sample of the allylic manganese compound rearranged spontaneously during a two week period, in the crystalline form stored at −20°, to the propenyl isomer. Rearrangement was rapid in the melt (complete in less than 5 min at 60°), in a concentrated chloroform solution (complete in less than 30 min in a 25% solution at 30°; complete in less than 5 min in a similar solution at 60°) but was slow in a dilute chloroform solution (less than 5% rearrangement detected by IR spectroscopy in a 5% chloroform solution at 30° for 3 days). It has not so far been possible to establish reproducible kinetics for the rearrangement process. Addition of tetraethylammonium fluoride, manganese carbonyl, or the product propenyl isomer, to a dilute chloroform solution did not induce rearrangement.

TABLE 4

CHEMICAL SHIFT δ (ppm)[a] OF CF_2 GROUP IN CF_2=CCl–CF_2G

G	δ	Ref.	G	δ	Ref.
I	40.4	17			
$Mn(CO)_5$	44.9	[b]	$As(CH_3)_2$	100.4	[b]
Cl	53.2	9	$PCl(C_6H_5)$	103.0	17
F	65.0	12	$P(CH_3)_2$	104.0	9
$PHCH{=}CHC_6H_5$	89.0	17	$P(O)Cl_2$	104.7	9
PHC_2H_5	89.4	9	$P(O)(C_6H_5)_2$	105.9	9
			$P(O)(Cl)C_6H_5$	106.1	17
PHC_6H_5	90.6	9	$P(O)(OCH_3)_2$	108.0	9
$PHCH_3$	91.6	9	$P(O)(OCH_3)C_6H_5$	109.1	17
$P(C_6H_5)_2$	94.7	9	H	117.5	17

[a] Upfield from internal $CFCl_3$. [b] Present work.

The stereochemistry of the rearranged products has been established by comparison of observed CF_3–F coupling constants with those established in model systems[12,13]. In the following discussion the terms *cis* and *trans* will refer to the relative positions of the CF_3 group and the G substituent in the compounds $CF_3CCl{=}CFG$. The observed ratios of *cis*- to *trans*-isomers are reported in Table 5, which also includes relevant NMR and IR data. Included in the table is the compound π-cyclopentadienyl-

TABLE 5

IR AND ^{19}F NMR DATA FOR $CF_3CCl{=}CFG$ COMPOUNDS

G	Stereochemistry	Percentage in mixture	$\nu(C{=}C)$ (cm^{-1})	$\delta(CF_3)$ (ppm)	$\delta(CF)$ (ppm)	$J(CF_3{-}C{=}CF)$ (Hz)	Other J (Hz)
$As(CH_3)_2$	*cis*	63	1620^a	63.8	94.0	7.4	
	trans	37		62.2	88.9	24.2	
$Mn(CO)_5$	*cis*(?)	5	1573^b	59.0		8.8	
	trans	95		60.3	25.5	24.3	
$Fe(CO)_2(\pi\text{-}C_5H_5)$	*cis*(?)	7	1564^b	58.0		8.7	
	trans	93		60.1	19.4	23.6	
$P(O)(OCH_3)_2$	*cis*	37	1628^b 1632^b	62.0	98.2	8.3	$J(FCP)$ 91.9 $J(CF_3P)$ 3.2
	trans	63		64.0	106.8	24.6	$J(FCP)$ 90.0 $J(CF_3P)$ 1.0
$P(C_6H_5)_2$	*cis*	50	1611^b 1618 (sh)	58.8	83.6	8.9	$J(FCP)$ 14.2 $J(CF_3P)$63.7
	trans	50		62.8	91.4	23.7	$J(FCP)$ 24.0 $J(CF_3P)$ 5.5

[a] *Gas phase.* [b] *Solution in* $CHCl_3$

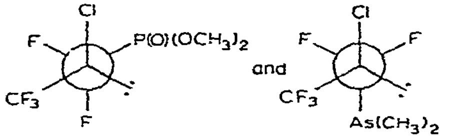
σ-(2-chlorotetrafluoropropenyl)iron dicarbonyl, which was isolated in low yield from the reaction between 2,3-dichlorotetrafluoropropene and the π-cyclopentadienyliron dicarbonyl anion. It was not possible to isolate an unrearranged allyl compound from this reaction, even with a mild work-up procedure. Presumably the allyl compound is formed, but is very easily rearranged.

In the rearrangements of the phosphorus and arsenic propenyl compounds, appreciable amounts of both *cis*- and *trans*-isomers are formed. However, both the manganese and iron compounds yield predominantly *trans*-isomer, as was earlier observed in an analogous system[5]. The tentative identification of a small percentage of *cis*-isomer rests, in each case, on the observation of a weak doublet in the ^{19}F NMR spectrum in the region expected for a $CF_3{-}C{=}C$ group, and with a splitting consistent with a *trans*-$CF_3C{=}CF$ arrangement. The quartet which should be observed for the CF group in this minor component was sought, but could not be found, perhaps because of signal-noise ratio problems.

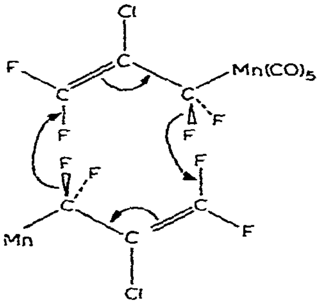
The stereochemical results for the arsenic and phosphorus systems are of interest in connection with mechanisms of nucleophilic substitution with rearrangement in highly halogenated allyl systems. There is evidence for a concerted S_N2^1 mechanism for some acyclic systems[11] while an intermediate carbanion has been suggested for some cyclobutenes[14]. In the systems studied here, with fluoride ion as a very reactive attacking nucleophile, but a poor leaving group[11], it would be reasonable to expect some preference for an intermediate carbanion, stabilized by the highly electronegative groups attached:

$$F^- + CF_2{=}CCl{-}CF_2G \rightarrow [CF_3{-}\bar{C}Cl{-}CF_2G] \rightarrow CF_3{-}CCl{=}CFG + F^-$$

If rotation within this carbanion were relatively fast compared with its lifetime, and there were no conformational preference, then *trans*-elimination of fluoride ion should give a 50 : 50 mixture of *cis*- and *trans*-propenyl compounds; this is the result observed (perhaps fortuitously) for (2-chlorotetrafluoroallyl)diphenylphosphine. For the dimethylarsine, and the phosphonate, the *cis*/*trans* ratios depart significantly from 50 : 50. This could indicate significant conformational preference in the intermediate carbanion, the preferred conformers being:



The stereochemical results in the rearrangement of the manganese compound (and in the presumed rearrangement of the iron compound) again point out the anomalous nature of this reaction. The almost exclusive *trans*-products indicate a highly constrained transition state for the reaction, while the qualitative kinetic results suggest an intermolecular reaction. These observations together with the IR observations above on the relative weakness of the C–F bond in the position adjacent to manganese suggest that in the (polyfluoroallyl)manganese compound there is an internal nucleophile already available for rearrangements—the relatively polar $\overset{\delta+}{\mathrm{C}}-\overset{\delta-}{\mathrm{F}}$ bond—and that the transition state for rearrangement may look something like the following:



It is clear from the results of rearrangement with both main group and transition element derivatives that the CF_3–CCl=CFG compounds are thermodynamically more stable than their CF_2=CCl–CF_2G isomers. Using some recently derived bond energy term values for chlorofluorocarbons[15] it may be calculated that when G = Cl or C (with unspecified attached groups), the heat of atomization of the propenyl compound is substantially higher (by over 10 kcal) than that of the allyl compound. No bond energy term values are available for the substituent groups studied in this work, but the qualitative result calculated with a chlorine or carbon substituent would probably be applicable to other substituents.

IR and NMR spectra of propenyl compounds

The most interesting feature of the infrared spectra (Table 5) is the frequency of the C=C stretching vibrations. In the dimethylpropenyl phosphonate 2 bands are apparent at 1632 and 1628 cm^{-1}, perhaps attributable to the *cis*- and *trans*-isomers.

Similarly, in the diphenylphosphine a shoulder at 1618 cm^{-1} appears on the main band at 1611 cm^{-1}. The dimethylarsine shows only one, somewhat broad, band at 1620 cm^{-1}. In the manganese derivative the C=C stretching frequency has dropped to 1570 cm^{-1} and a similar band occurs at 1564 cm^{-1} in the iron compound. These lower frequencies of the transition metal compounds indicate a distinct weakening of the carbon–carbon bond, presumably with a concomitant strengthening of the carbon–metal bond:

$$C{=}C{-}M \leftrightarrow C{-}C{=}M$$

The ^{19}F NMR spectra (Table 5) show a downfield shift of some 60 or more ppm for the =CF–G nuclei in the iron and manganese compounds. There is too little data, however, to warrant extensive discussion of this observation.

EXPERIMENTAL

All reactions were conducted in a nitrogen atmosphere unless otherwise stated. Arsines were manipulated in a vacuum line of standard design, equipped throughout with needle valves made of fluorocarbon polymer. 2,3-Dichlorotetrafluoropropene and the (2-chlorotetrafluoroallyl)phosphorus compounds were prepared by published methods[9]. Other reagents and solvents were commercial samples purified by standard methods. IR spectra were recorded on a Beckman IR-12 spectrophotometer; ^1H NMR spectra were determined on a Varian A-60 instrument, and ^{19}F NMR spectra on a Varian A-56/60 instrument.

Dimethylarsine

In a 3-necked 1-l flask, equipped with dropping funnel and stirrer, and connected to traps cooled in solid CO_2 and liquid N_2, were placed 32 g (0.2 mole) of sodium cacodylate, 39 g (0.6 mole) of zinc powder, 0.5 g mercury(II) chloride, 75 ml of water and 175 ml ethanol. The mixture was stirred and 200 ml of concentrated HCl was added dropwise. The volatile materials were transferred from the traps to the vacuum line and distilled slowly through traps at −78°, −112° and −196°. The material collecting at −112° was dimethylarsine (0.13 mole, 65%) characterized by IR and ^1H NMR spectra.

(2-Chlorotetrafluoroallyl)dimethylarsine

A mixture of 0.103 mole of dimethylarsine and 0.103 mole of 2,3-dichlorotetrafluoropropene was sealed in a thick-walled 500 ml tube and held at room temperature for 4 weeks. The contents of the tube were transferred to a vacuum line and fractionated through traps at −47°, −78°, and −196°. The material condensing at −196° was hydrogen chloride (0.0425 mole); that condensing at −47° was (2-chlorotetrafluoroallyl)dimethylarsine (0.059 mole, 57%) b.p. 105° (extrapolated). (Found: C, 24.0; H, 2.6; As, 29.3; mol.wt. gas vapor density, 248. $C_5H_6AsClF_4$ calcd.: C, 23.7; H, 2.4; As, 29.6%; mol.wt. 252.4.) The residual involatile material in the tube was not characterized.

(2-Chlorotetrafluoroallyl)manganese pentacarbonyl

A solution of excess 2,3-dichlorotetrafluoropropene (5.0 g, 27.2 mmoles) in

25 ml of tetrahydrofuran was added at room temperature to a solution of sodium manganese pentacarbonyl in 50 ml of tetrahydrofuran, prepared by a published method[16] from sodium amalgam (0.45 g Na in 5 ml Hg) and manganese carbonyl (3.0 g, 7.7 mmoles). The solution was filtered and solvent and excess olefin were removed from filtrate at, or below, 30°. The residue was sublimed in vacuo (40°/0.1 mm) to yield colorless crystals of (2-chlorotetrafluoroallyl)manganese pentacarbonyl (3.1 g, 9.0 mmoles, 59%) m.p. 47–48° (Found: C, 28.2; H, 0.0; Mn, 16.0. $C_8ClF_4MnO_5$ calcd.: C, 28.0; H, 0.0; Mn, 16.0%.)

(2-Chlorotetrafluoropropenyl)dimethylarsine

Cesium fluoride (0.5 g) and (2-chlorotetrafluoroallyl)dimethylarsine (6 mmoles) were held in a sealed 5 ml tube for 4 weeks at 30°. The volatile materials were taken into a vacuum line and condensed in a −47° trap to yield (2-chlorotetrafluoropropenyl)dimethylarsine (5.5 mmoles, 91%) b.p. 100° (extrapolated). (Found: As, 29.4; mol. wt. gas vapor density, 250. $C_5H_6AsClF_4$ calcd.: As, 29.6%; mol. wt., 252.4.)

(2-Chlorotetrafluoropropenyl)manganese pentacarbonyl

A 1.0 g sample of (2-chlorotetrafluoroallyl)manganese pentacarbonyl was held in a sealed tube at 55° for 5 min, when it solidified. The product was sublimed (60°/0.1 mm) to yield (2-chlorotetrafluoropropenyl)manganese pentacarbonyl (0.9 g, 90%) m.p. 66–68°. (Found: C, 28.5; H, 0.0. $C_8ClF_4MnO_5$ calcd.: C, 28.0; H, 0.0%.)

π-Cyclopentadienyl-σ-(2-chlorotetrafluoropropenyl)iron dicarbonyl

Cyclopentadienyliron dicarbonyl dimer (5.3 g, 15 mmoles) in tetrahydrofuran (80 ml) was stirred with sodium amalgam (0.9 g Na in 7 ml Hg) for 2 h at 30°. Excess amalgam was removed and a solution of 2,3-dichlorotetrafluoropropene (6.6 g, 36 mmoles) in tetrahydrofuran (25 ml) was added dropwise. After 30 min the mixture was filtered and volatile materials were removed from the filtrate under reduced pressure. The residue was dissolved in benzene (30 ml) and applied to a column of acid washed chromatography grade alumina (15 mm × 150 mm) being eluted with petroleum ether. The first (yellow) band was the propenyl derivative (0.4 g, 1.2 mmoles, 4%) characterized solely by its spectral properties. The second (red) band was cyclopentadienyliron dicarbonyl dimer.

(2-Chlorotetrafluoropropenyl)diphenylphosphine

Cesium fluoride (0.5 g) and (2-chlorotetrafluoroallyl)diphenylphosphine (3.0 g) were heated *in vacuo* at 100° for 8 h. The product was distilled to yield (2-chlorotetrafluoropropenyl)diphenylphosphine (2.0 g, 67%) b.p. 105–115°/0.01 mm. (Found: C, 54.9; H, 3.9. $C_{13}H_{10}ClF_4P$ calcd.: C, 54.2; H, 3.0%.)

Dimethyl (2-chlorotetrafluoropropenyl)phosphonate

Cesium fluoride (0.5 g) was added to dimethyl (2-chlorotetrafluoroallyl)-phosphonate (5.0 g) at room temperature. There was a mild initial reaction which was completed by heating the mixture at 60° for 1 h. Distillation yielded dimethyl (2-chlorotetrafluoropropenyl)phosphonate (3.8 g, 76%) b.p. 35–45°/0.01 mm. (Found: C, 23.3; H, 2.6. $C_5H_6ClF_4O_3P$ calcd.: C, 23.4, H, 2.3%.) This material was separated by gas chromatography on a $20' \times \frac{3}{8}''$ column, with stationary phase 10% SE/30 silicone oil on chromosorb at 195°. The first fraction, elution volume 1500 ml He, was identified by ^{19}F NMR spectroscopy as the *trans*-isomer, and the second fraction, elution volume 1620 ml He, as the *cis*-isomer.

ACKNOWLEDGEMENTS

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