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THE PREPARATION AND REACTIONS OF GROUP IIB METAL CHLORIDE STABILIZED COMPLEXES OF (CHLOROFLUOROMETHYLENE)TRIS(DIMETHYLAMINO)PHOSPHORANE

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Summary

A facile dechlorination reaction occurs between $[((CH_3)_2N)_3{}^+PCFCl_2]Cl^-$ and Group IIB metals to form addition complexes of the type $[((CH_3)_2N)_3P^+CFCl(MCl)]Cl^-$ where M = Zn, Cd, or Hg. These complexes exhibit surprising stability in ethereal solvents, and serve as effective 1-chloro-1-fluorovinyl transfer agents via the Wittig reaction by dissociation into $[(CH_3)_2N]_3P{=}CFCl$ and the metal chloride. ^{19}F and ^{31}P NMR, as well as derivative formation, substantiate that these complexes are indeed quaternary phosphonium compounds which contain covalent carbon—metal bonds.

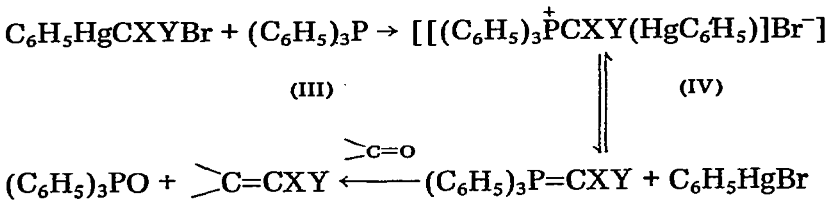
Introduction

Phosphorus ylides are powerful donor molecules as evidenced by their numerous reactions with Lewis acids [1—3]. Those resultant complexes which specifically exhibit Wittig reactivity toward carbonyl compounds are called "quasicomplexes" [4]. They represent a rather diverse group of compounds as a result of the large number of combinations possible [5—8].

Several workers have investigated the direct, or suspected intermediate reaction of methylene ylides with Group IIIB metal halides. Seyferth et al. [9,10] have reported that reaction of methylenetriphenylphosphorane (I) with mercuric bromide results in the formation of a stable, isolable complex (II) which has not been structurally elucidated.

$$\underset{\text{(I)}}{(C_6H_5)_3P{=}CH_2} + \text{excess } HgBr_2 \rightarrow \underset{\text{(II)}}{[[(C_6H_5)_3\overset{+}{P}CH_2]_2Hg][HgBr_3]_2{}^-} \tag{1}$$

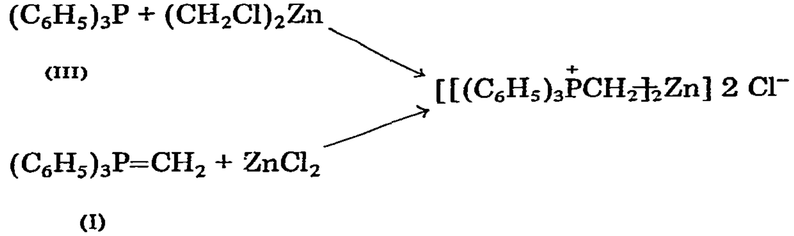
Their subsequent work [11,12] involving triphenylphosphine (III) assisted decomposition of mercurials provided a convenient synthetic route to 1-haloolefins. Mechanistic studies suggested the intermediacy of an ylide—phenylmercuric bromide complex (IV) which dissociates to afford the reactive methyler species and phenylmercuric bromide.



$$\begin{tikzcd}[column sep=small] C_6H_5HgCXYBr + (C_6H_5)_3P \text{ (III)} \arrow[r] & {[[(C_6H_5)_3\overset{+}{P}CXY(HgC_6H_5)]Br^-]} \text{ (IV)} \arrow[d, shift left] \\ (C_6H_5)_3PO + {>}C{=}CXY & (C_6H_5)_3P{=}CXY + C_6H_5HgBr \arrow[u, shift left] \arrow[l, ">C=O"'] \end{tikzcd} \qquad (2)$$

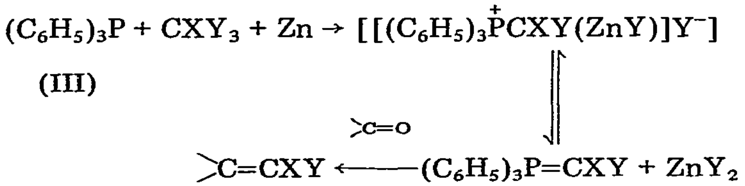
(X = Y = Cl, Br; X = H, Y = Br, Cl)

Strikingly similar results have been obtained when other Group IIB members have been employed. Although workers have paid scant attention to cadmium [13], zinc has been found to react in a manner very similar to mercury. Wittig and Schwarzenbach [14] reported the preparation of an isolable zinc chloride analogue of II, resulting from the reaction of III with bis(chloromethyl)zinc, or alternatively, from a direct interaction of I with zinc chloride.



$$\begin{tikzcd}[column sep=small] \underset{\text{(III)}}{(C_6H_5)_3P} + (CH_2Cl)_2Zn \arrow[dr] & \\ & {[[(C_6H_5)_3\overset{+}{P}CH_2]_2Zn]\ 2\ Cl^-} \\ \underset{\text{(I)}}{(C_6H_5)_3P{=}CH_2} + ZnCl_2 \arrow[ur] & \end{tikzcd} \qquad (3)$$

Several workers have since reported the use of zinc in Wittig olefination schemes, each of which presumably proceeds through some type of ylide—zinc halide quasicomplex. Of the major approaches, the first involves a "one-pot" reaction of III with an appropriate perhalomethane and zinc dust in the presence of a carbonyl containing compound.



$$\begin{tikzcd}[column sep=small] \underset{\text{(III)}}{(C_6H_5)_3P} + CXY_3 + Zn \arrow[r] & {[[(C_6H_5)_3\overset{+}{P}CXY(ZnY)]Y^-]} \arrow[d, shift left] \\ {>}C{=}CXY & (C_6H_5)_3P{=}CXY + ZnY_2 \arrow[u, shift left] \arrow[l, ">C=O"'] \end{tikzcd} \qquad (4)$$

(X = Y = Br [15]; X = F, Y = Cl [16])

The second method involves the dehalogenation of an isolated phosphonium salt [17,18]. The resulting ylide—zinc iodide complex (V) exhibits greater stability, but a lesser reactivity than its free ylide counterpart, affording higher olefin yields from aldehydes and activated ketones, but lower yields from unactivated ketones such as acetophenone [18].

$$\begin{array}{l} [(C_6H_5)_3\overset{+}{P}CHFI]I^- + Zn(Cu) \xrightarrow[0^\circ C]{DMF} \underset{(V)}{[(C_6H_5)_3\overset{+}{P}CHF(ZnI)]I^-} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \upharpoonleft\!\downharpoonright \\ \underset{12\%}{E + Z\ C_6H_5(CH_3)C{=}CHF} \xleftarrow{C_6H_5(CH_3)C{=}O} (C_6H_5)_3P{=}CHF + ZnI_2 \end{array} \qquad (5)$$

This report describes the preparation of stable chlorofluoromethylene ylide—Group IIB metal chloride complexes. They exhibit a surprisingly wide scope of reactivity with carbonyl compounds, and provide an important new synthetic route to chlorofluoromethylene olefins. Structural elucidation of these reactive intermediates is achieved by ^{19}F and ^{31}P NMR, as well as elemental analysis of several Lewis acid derivatives. These quasicomplexes, as well as their derivatives, are quatervalent phosphonium compounds which are composed of a 1/1 ratio of ylide : metal chloride.

Results and discussion

Synthetic scope

Several years ago Van Wazer et al. [19] reported ^{31}P NMR data for (dichlorofluoromethyl)tris(dimethylamino)phosphonium chloride (VI). It proved convenient to prepare VI from a direct reaction of tris(dimethylamino)phosphine (VII) with trichlorofluoromethane at 0°C,

$$\underset{(VII)}{((CH_3)_2N)_3P} + CFCl_3 \xrightarrow[0^\circ C]{Et_2O} \underset{(VI)}{[((CH_3)_2N)_3\overset{+}{P}CFCl_2]Cl^-} \qquad (6)$$

We found that zinc—copper couple exothermally dechlorinates VI in the presence of carbonyl compounds to afford good yields of 1-chloro-1-fluoromethylene olefins.

$$[((CH_3)_2N)_3\overset{+}{P}CFCl_2]Cl^- + Zn(Cu) + \ {>}C{=}O \xrightarrow{60^\circ C} {>}C{=}CFCl + [(CH_3)_2N]_3PO + ZnCl_2 \qquad (7)$$

A solvent survey conducted with acetophenone as the model carbonyl compound indicated that ethereal solvents, such as THF, afforded higher olefin yields than polar aprotic solvents such as DMF or benzonitrile (Table 1).

TABLE 1

SOLVENT SURVEY

$[((CH_3)_2N)_3\overset{+}{P}CFCl_2]Cl^- + Zn(Cu) + C_6H_5C(O)CH_3 \xrightarrow{60^\circ C} C_6H_5(CH_3)C{=}CFCl\ (E + Z)$

Solvent	Reaction duration (h) [a]	Olefin yield (%) [b]	*E*/*Z*
THF	4.5	70	52/48
Triglyme	5	72	50/50
DMF	3.5	36	48/52
CH_3CN	2	11	53/47
C_6H_5CN	2	55	49/51

[a] Time at which maximum olefin yield is first realized. [b] GLPC yield based on starting acetophenone.

TABLE 2

METAL DECHLORINATION SURVEY

$$[((CH_3)_2N)_3\overset{+}{P}CFCl_2]Cl^- + M + C_6H_5C(O)CH_3 \xrightarrow[60^\circ C]{THF} C_6H_5(CH_3)C{=}CFCl\ (E + Z)$$

M	Reaction duration (h) [a]	Olefin yield (%) [b]	*E*/*Z*
Zn	3	75	48/52
Zn/Cu	4.5	70	52/48
Zn/Hg	3.5	69	50/50
Zn/Cu/Hg	4	66	49/51
Cd	15 [c]	66	47/53
Cd/Hg	4	43	47/53
Hg [d]	49.5 [c]	12	51/49

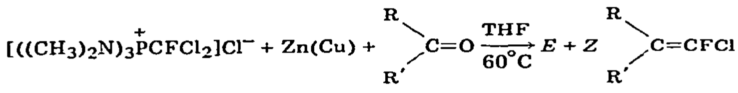
[a] Time at which maximum olefin yield is first realized. [b] GLPC yield based on starting acetophenone. [c] When reaction was terminated. [d] Acetonitrile utilized as reaction solvent.

In a further optimization of reaction conditions, the dechlorination abilities of other Group IIB metals or metal amalgams were investigated (Table 2). Although zinc dust proved to be as active as zinc—copper couple, the latter was routinely employed in all subsequent olefinations as it did not exhibit the uncontrollable induction periods characteristic of zinc dust. Mercury proved to be ineffective when THF served as reaction solvent.

Table 3 lists the results obtained from the carbonyl survey. Although aldehydes are quantitatively converted to olefins, unactivated ketones afford much lower yields. This trend has been consistently observed by all workers who have attempted to prepare chlorofluoromethylene olefins by a Wittig approach [16]. However, the present synthetic approach is the method of choice because of its high conversion of most carbonyl compounds. In addition, the ready availability of starting materials, ease of reaction scale up, nonbasic reaction conditions, and ease of product isolation is unsurpassed. The latter is particularly important

TABLE 3

CARBONYL SURVEY



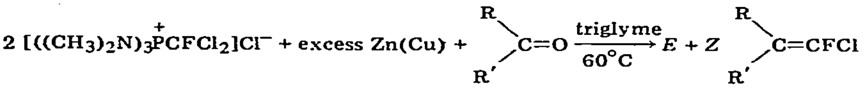
$$[((CH_3)_2N)_3\overset{+}{P}CFCl_2]Cl^- + Zn(Cu) + RR'C{=}O \xrightarrow[60^\circ C]{THF} E + Z\ RR'C{=}CFCl$$

R	R'	Reaction duration (h) [a]	Olefin yield (%) [b]	*E*/*Z*
C_6H_5	CF_3	1	100	44/56
C_6H_5	H	1	100	47/53
C_6H_{13}	H	0.5	100	59/51
C_6H_5	CH_3	4.5	70	52/48
CF_3 [c]	CF_3	1.5	75	
$-CH_2CH_2CH_2CH_2-$		25 [d]	18	
C_6H_5	C_6H_5	28 [d]	0	

[a] Time at which maximum olefin yield is first realized. [b] GLPC yield based on starting carbonyl compound. [c] Reaction at 0°C in triglyme. [d] When reaction was terminated.

TABLE 4

REACTION OF THE (DICHLOROFLUOROMETHYL)TRIS(DIMETHYLAMINO)PHOSPHONIUM CHLORIDE ZINC—COPPER SYSTEM WITH ACTIVATED ESTERS AND AMIDES



$$2\,[((CH_3)_2N)_3\overset{+}{P}CFCl_2]Cl^- + \text{excess } Zn(Cu) + \overset{R}{\underset{R'}{>}}C{=}O \xrightarrow[60^\circ C]{\text{triglyme}} E + Z \quad \overset{R}{\underset{R'}{>}}C{=}CFCl$$

R	R′	Reaction duration (h) [a]	Olefin yield (%) [b]	*E*/*Z*
CF_3 [c]	OC_3H_7-i	19.5	51	<0.1
CF_3	OCH_3	30	90	<0.1
CF_2Cl	OCH_3	17.5	71	<0.1
$CFCl_2$ [d]	OCH_3	30	0	
CF_2H	OCH_3	30	23	<0.1
C_2F_5	OC_2H_5	15	22	<0.1
C_3F_7	OCH_3	46	21	[e]
CF_3	$N(CH_3)_2$	19	0	

[a] When reaction was terminated. [b] ^{19}F NMR yield based on starting carbonyl compound. [c] Ratio of $[((CH_3)_2N)_3PCFCl_2]Cl^-/CF_3CO_2C_3H_7$-i = 1.33. [d] Utilized a pregenerated, filtered olefinating solution. [e] Not possible to make an unambiguous stereochemical assignment; only one vinyl fluorine absorption detected.

as the necessity of steam distillation is avoided as triphenylphosphine oxide is not a reaction product [20—22].

The general isolation procedure involves filtration of the reaction solution into a separatory funnel, followed by water washings and ether extraction. Drying of the extract, followed by simple vacuum distillation affords the product chlorofluoromethylenes, which may then be separated by preparative GLPC or spinning band distillation.

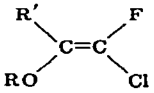
Esters were also found to be reactive, affording good yields of fluorinated vinyl ethers (Table 4). Variance of substitution at the trifluoromethyl site of methyl trifluoroacetate suggests that the applicability of this olefination approach is strictly limited to highly activated esters. Only two other reports describe the preparation of fluorinated vinyl ethers via a Wittig route [23,24]. However, this method is somewhat different in that those reports describe the reaction of monofluoro- or trifluoroethylacetates with (alkylidene)triphenylphosphoranes. As expected, an activated amide was found to be unreactive.

Unfortunately, it proved impossible to isolate the prepared vinyl ethers because of an unexpected polymerization which occurred during solvent removal prior to work up. However, all reaction products were identified by comparison of their ^{19}F NMR data (Table 5) to that reported for *cis*- and *trans*-3-methoxyperfluoro-2-pentene, which were prepared by an alternate route [25].

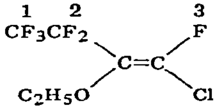
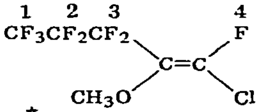
It is indeed puzzling that the *E*/*Z* isomer ratio is so small in these cases, when it should be anticipated to approach unity as observed for those members of Table 3. Close examination of Table 4 reveals that electronic effects, as well as steric factors at the alkyl or alkoxy site of the ester, are not important. Vinyl ethers, when prepared by other methods [25,26], afford an isomer ratio close to unity. Furthermore, both isomers in each reaction system were reported to

TABLE 5

^{19}F NMR DATA FOR 1-CHLORO-1-FLUOROVINYL ETHERS

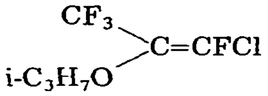


R	R′	Isomer	ϕ^*(R′) (ppm)	ϕ^*(vinyl F) (ppm)	$J(^{19}F(vinyl)—R')$ (Hz)
CH_3	CF_3	*Z*	65.1	96.4	24.2
i-C_3H_7	CF_3	*Z*	64.1	96.7	21.3
CH_3	CF_2Cl	*Z*	52.9	94.8	34.0
CH_3	CF_2H	*Z*	120.8	92.5	15.0 [a]
C_2H_5	C_2F_5	*Z*	[b]	93.6	[b]
CH_3	C_3F_7	*Z*	[c]	115.0	[c]

[a] $J(^{19}F(vinyl)—^1H) \simeq 0$ Hz. [b]  $\phi_1^* = 83.4$, dt (CF_3); $J_{1,2} = 2.8$ Hz, $J_{1,3} = 6.8$ Hz; $\phi_2^* = 116.1$ dq (CF_2); $J_{2,3} = 29.9$ Hz; $\phi_3^* = 93.6$ tq (vinyl F). [c]  $\phi_1^* = 81.3$, t (CF_3); $J_{1,3} = 7.4$ Hz; $\phi_2^* = 120.0$, m (CF_2); $\phi_3^* = 127.5$, m (allylic CF_2); $\phi_4^* = 115.0$, m (vinyl F). Impossible to unambiguously assign stereochemistry due to diluteness of sample; only one vinyl fluorine absorption detected.

be stable at reaction temperatures (<85°C), suggesting that thermally-induced isomer interconversion does not occur.

Additional reactions involving phosphine dechlorination of VI were conducted in the presence of isopropyl trifluoroacetate in order to examine the resulting stereochemistry arising from reaction of the ester with uncomplexed chlorofluoromethylene ylide.



$$[((CH_3)_2N)_3\overset{+}{P}CFCl_2]Cl^- + R_3P + CF_3CO_2C_3H_7\text{-i} \rightarrow (CF_3)(i\text{-}C_3H_7O)C{=}CFCl \quad (8)$$

(VIII)

(VIII, R = C_6H_5, 40%; VIII, R = $(CH_3)_2N$, 65%)

Good yields of 1-chloro-2-isopropoxyperfluoropropene (VIII) were obtained in each case, ester cleavage by the dichlorophosphorane competing ineffectively [27]. The stereochemistry of both reactions was essentially identical, with an exclusive preference for the *Z* isomer. Preferential betaine collapse, which has been reported present in other Wittig systems [1,28], cannot be ruled out as the explanation for this phenomenon.

Nature of the olefinating intermediates

(1) Stability. During the course of this work, it was noted that olefination

of unreactive carbonyls at 60°C in THF continued slowly, often requiring several hours. Previous reports describing the stabilities of fluoro- and (chlorofluoromethylene)triphenylphosphoranes [29,30] indicated that both are stable for only short periods at room temperature. Furthermore, chemical intuition would suggest that tris(dimethylamino) analogues would exhibit even less stability because of donation of electron density from the dimethylamino-nitrogens to the ylide phosphorus.

Dechlorination of VI in THF at 60°C was next conducted in the absence of carbonyl compounds in order to directly examine the stability of the olefinating intermediate. Zinc—copper couple immediately and exothermically reacted with VI, while cadmium exhibited an induction period; mercury was essentially unreactive. Addition of benzaldehyde to those pregenerated intermediates, followed by ^{19}F NMR examination indicated that the zinc-derived quasicomplex was stable for over ten hours under reaction conditions (60°C), whereas the cadmium analogue was unreactive after two hours. In a separate stability study, the filtered, dark brown reaction solution resulting from zinc dechlorination of VI in THF at 60°C exhibited reactivity towards benzaldehyde for nearly 30 days when stored at room temperature. This represents an unparalleled feat for a methylene type ylide, and definitely suggests the presence of an intermediate stabilized ylide complex.

When the stability studies were repeated in benzonitrile, the metal-derived intermediates were stable in the order Hg $\gg$ Zn $\simeq$ Cd. The complex obtained from the dechlorination of VI by mercury formed slowly, but exhibited reactivity with benzaldehyde after 83 hours at 60°C. In contrast, the zinc generated intermediate was stable for two hours, and the cadmium for less than one hour under similar reaction conditions.

(2) NMR characterization. ^{19}F spectral examination of the filtered THF reaction solution obtained from zinc-copper couple dechlorination of VI revealed no remaining VI, but instead a species exhibiting a signal (doublet) at $\phi^* = 149.7$, $J(^{19}\mathrm{F}—^{31}\mathrm{P}) = 67.0$ Hz. Subsequent addition of benzaldehyde caused a disappearance of this absorption and appearance of signals attributable to *E*- and *Z*-β-chloro-β-fluorostyrene. The ^{19}F data of VI, as well as the zinc-generated quasicomplex, is presented in Table 6. The covalency of the phosphorus atom in each compound shows no solvent dependency, a behavior characteristic of di- or perhalomethylphosphonium halides [30]. This evidence strongly suggests the intermediate zinc quasicomplex (IX) is a quaternary phosphonium compound.

$$\underset{\text{(VI)}}{[((\mathrm{CH_3})_2\mathrm{N})_3\overset{+}{\mathrm{P}}\mathrm{CFCl_2}]\mathrm{Cl}^-} + \mathrm{Zn(Cu)} \xrightarrow[60^\circ\mathrm{C}]{\mathrm{THF}} \underset{\text{(IX)}}{[((\mathrm{CH_3})_2\mathrm{N})_3\overset{+}{\mathrm{P}}\mathrm{CFCl(ZnCl)}]\mathrm{Cl}^-} \tag{9}$$

In order to substantiate the covalency of the carbon—metal bond in the intermediate quasicomplexes, VI was dechlorinated by either cadmium or mercury in benzonitrile in the absence of carbonyl compounds. The ^{19}F NMR data of each complex is reported in Table 7; each absorption has been unequivocally assigned to the intermediate quasicomplex by observing its subsequent disappearance after addition of benzaldehyde. The satellite peak data is characteristic of a *geminal* F—C—M structure within the cadmium (X) and mercury

TABLE 6

^{19}F NMR DATA OF $[((CH_3)_2N)_3\overset{+}{P}CFClX]Cl^-$ IN VARIOUS SOLVENTS

X	Solvent	ϕ^* (ppm) [a]	$J(^{19}F—^{31}P)$ (Hz)
Cl	DMF	58.8	83.7
Cl	DMSO	58.8	82.3
Cl	CH_3CN	58.6	83.5
Cl	H_2O	59.9 [b]	83.8
Cl	EtOH	59.3	83.6
ZnCl	DMF	149.9	65.6
ZnCl	C_6H_5CN	148.4	67.4
ZnCl	THF	149.7	67.0
ZnCl	Dioxane	148.5	67.5
ZnCl	Triglyme	149.9	66.5

[a] Upfield from internal $CFCl_3$. [b] External $CFCl_3$.

(XI) complexes; indeed, these intermediates are truly organometallic compounds.

$$[((CH_3)_2N)_3\overset{+}{P}CFCl_2]Cl^- + M \xrightarrow[60^\circ C]{C_6H_5CN} [((CH_3)_2N)_3\overset{+}{P}CFCl(MCl)]Cl^- \qquad (10)$$

(VI)

(X) M = Cd; (XI) M = Hg

In addition, the magnitude of the $J(^{19}F—^{31}P)$ indicates the existence of a *geminal* F—C—P system [30]. Consideration of the $J(^{19}F—^{199}Hg)$ value suggests it is well within the range reported for bis(perfluoroalkyl)mercury compounds [31,32], as well as fluorinated mercurials [33,34].

(3) Derivative formation. Isolation of IX was attempted in order to further elucidate its structure. Vacuum distillation of THF from a zinc-generated, filtered reaction solution afforded a large amount of a brown, viscous, noncrystallizing oil. Readdition of solvent yielded a solution capable of olefinating benzaldehyde. However, other, more indirect approaches proved to be much more successful.

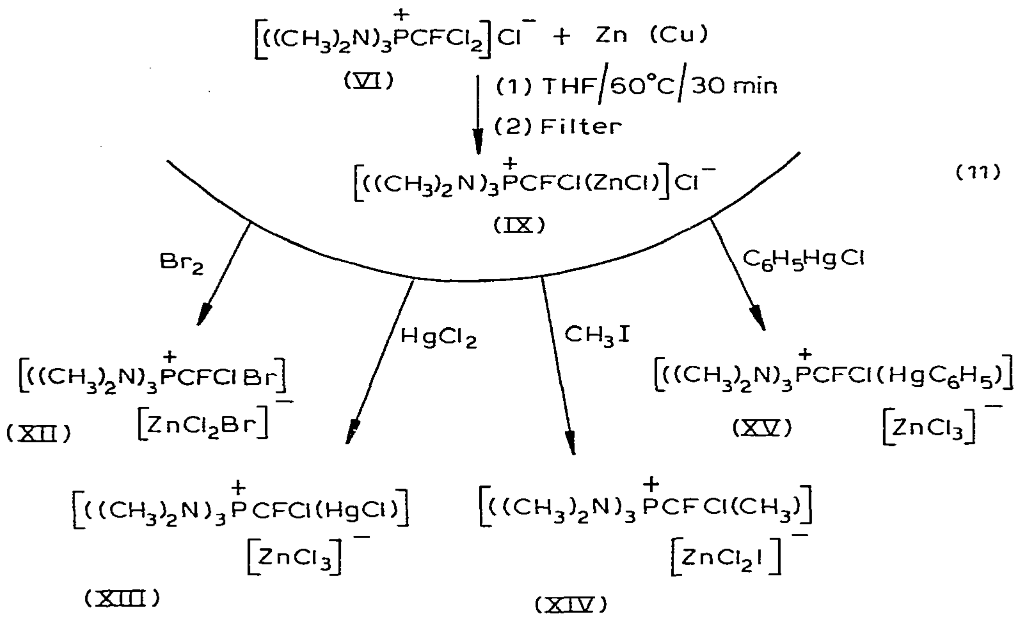
Bromine, mercuric chloride, methyl iodide, and phenylmercuric chloride were added to separate, filtered reaction solutions of IX in THF. Precipitates or oils were obtained in all cases, however satisfactory elemental analyses were obtained only from the bromine (XII) and mercuric chloride (XIII) adducts.

TABLE 7

^{19}F NMR DATA OF $[((CH_3)_2N)_3\overset{+}{P}CFCl(MCl)]Cl^-$ IN BENZONITRILE

M	ϕ^* (ppm) [a]	$J(^{19}F—^{31}P)$ (Hz)	$J(^{19}F—M)$ (Hz)
Zn	148.4	67.4	
Cd	147.3	67.6	145
Hg	126.3	65.9	698

[a] Upfield from internal $CFCl_3$.



(11)

The ^{19}F NMR data for XII—XV are reported in Table 8. The anions of XII and XIII were verified by elemental analyses, and it is anticipated that similar trihalozinc counter ions are also present in XIV and XV. All adducts are mono(ylide) complexes based on the multiplicity of $J(^{19}F—^{31}P)$ values, elemental analysis, and reaction stoichiometry, however earlier reports [10,14,35] suggest that bis(ylide)metal complexes can be prepared in the cases of IX and XIII if an excess of metal halide is present. The possibility remains, however, that IX and/or XIII and XV may be other than monomeric species, although the high basicity of the methylene ylide itself would tend to support a monomeric intermediate [36].

^{31}P NMR was also used to advantage to more firmly establish the valence of phosphorus within these compounds. Workers in the past have attempted to correlate ^{31}P NMR chemical shifts with phosphorus covalency. Phosphines generally lie to the upfield side of external phosphoric acid (NMR reference

TABLE 8

^{19}F NMR DATA OF $[((CH_3)_2N)_3\overset{+}{P}CFClZnCl]Cl^-$ AND ITS DERIVATIVES IN THF

Compound	ϕ^* (ppm) [a]	$J(^{19}F—^{31}P)$ (Hz)	$J(^{19}F—M)$ (Hz)
IX	149.7	67.0	
XII	61.3	73.1	
XIII	127.0	67.9	717
XIV	100.1	84.6	[b]
XV	132.3	65.9	363

[a] Upfield from internal $CFCl_3$. [b] $J(^{19}F—^1H) = 23.0$ Hz.

TABLE 9

^{31}P NMR DATA OF $[((CH_3)_2N)_3\overset{+}{P}CFCl_2]Cl^-$ AND ITS DERIVATIVES

Compound	Solvent	ϕ^* (ppm) [a]	$J(^{31}P-^{19}F)$ (Hz)
VI	$CDCl_3$	—43.5	84.2
IX	Dioxane/C_6D_6	—50.3	64.7
XII	Acetone-d_6	—44.2	83.1
XIII	DMSO-d_6	—48.9	61.0 [b]
XIV	DMSO-d_6	—45.1	84.2 [c]

[a] Downfield from external H_3PO_4. [b] $J(^{31}P-^{199}Hg) = 664$ Hz. [c] Proton decoupled.

compound) while quaternary phosphonium halides lie within the —20 to —40 ppm range [37], although tris(dimethylamino)phosphonium salts extend the range to —63 ppm [19]. Ylide absorbances lie even farther downfield; ^{31}P NMR chemical shifts for methylene- and (ethylidene)tris(dimethylamino)-phosphoranes are —70.8 ppm and —64.5 ppm, respectively [38]. ^{31}P NMR data for several phosphonium compounds prepared in this report are presented in Table 9. These compounds exhibit NMR spectra which suggest they are quaternary phosphonium compounds.

Mechanism of olefination

Three observations suggest the active olefination intermediate is the free chlorofluorophosphonium ylide and not the observed quasicomplexes.

(1) Reaction product stereochemistry. The *E/Z* ratio of product propenes obtained from the olefination of acetophenone (Table 2) is similar, regardless of whether zinc, cadmium, or mercury is employed to dechlorinate VI. In addition, the stereochemistry of olefins obtained from simple aldehydes and activated ketones (Table 3) agrees closely with reports in which the free (chlorofluoromethylene)triphenylphosphorane is the actual olefination agent [20,21,39].

(2) Quasicomplex stability. The fact that IX and X are much more stable in ethereal solvents than in polar aprotic solvents suggests the existence of a dissociative equilibrium between the quasicomplex and the free ylide and metal chloride.

$$[((CH_3)_2N)_3\overset{+}{P}CFCl(MCl)]Cl^- \rightleftharpoons \underset{\text{(XVI)}}{((CH_3)_2N)_3P{=}CFCl} + MCl_2 \tag{12}$$

(M = Zn, Cd)

In each case, however, the equilibrium lies far to the left as no XVI is observed via ^{19}F NMR. This dissociative scheme is well documented for a series of mercuric chloride-stabilized ylide complexes [40].

(3) Metal exchange reactions. Elemental analysis and ^{19}F NMR evidence indicates that mercury can easily displace zinc or cadmium in IX or X, respectively, by simple addition of mercuric chloride to the appropriate filtered reaction solution.

$$\begin{tikzcd} {[((CH_3)_2N)_3\overset{+}{P}CFCl_2]Cl^- + M} \arrow[r, "C_6H_5CN", "60^\circ C"'] & {[((CH_3)_2N)_3\overset{+}{P}CFCl(MCl)]Cl^-} \arrow[dd, "HgCl_2"] \\ (VI) & \\ (M = Zn, Cd) & {[((CH_3)_2N)_3\overset{+}{P}CFCl(HgCl)][MCl_3]^-} \end{tikzcd} \qquad (13)$$

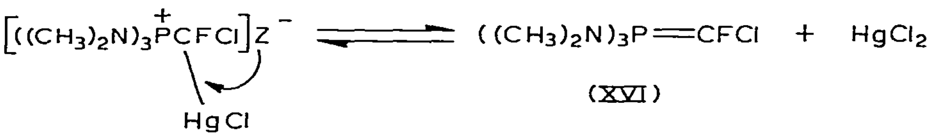
In each case, the ^{19}F NMR signals attributable to IX or X disappear after addition of mercuric chloride, and a doublet at $\phi^* \simeq 125$ ppm, $J(^{19}F—^{31}P) \simeq 68$ Hz, $J(^{19}F—^{199}Hg) \simeq 710$ Hz appears. This spectral data is undoubtedly that for XI (Table 7) as ^{19}F NMR chemical shift and coupling constant data for quaternary phosphonium compounds shows little dependence on solvent or counter ion [30].

In order to demonstrate the existence of this dissociative equilibrium, XIII was prepared from IX in THF as indicated in eq. 11. The heterogeneous reaction solution was divided into two aliquots, and benzaldehyde and dry sodium iodide were then added to the first. ^{19}F NMR analysis later indicated a good yield of the anticipated chlorofluorostyrenes, via olefination by XVI, which was generated by iodide ion cleavage of the carbon—mercury bond, a relatively facile process [11,12,41,42].

$$\begin{tikzcd} & {\begin{array}{c}[((CH_3)_2N)_3\overset{+}{P}CFCl(HgCl)][ZnCl_3]^- \\ (XIII)\end{array}} \arrow[dl, "\begin{array}{l}(1)\ C_6H_5CHO/NaI \\ (2)\ 6\ h/50^\circ C\end{array}"'] \arrow[dr, "\begin{array}{l}(1)\ —THF \\ (2)\ C_6H_5CN/C_6H_5CHO \\ (3)\ 3\ h/75^\circ C\end{array}"] & \\ E + Z\ C_6H_5C(H)=CFCl & & \text{trace olefination} \end{tikzcd} \qquad (14)$$

Meanwhile, the second aliquot was subjected to vacuum distillation, followed by addition of dry benzonitrile. Subsequent addition of benzaldehyde was followed by prolonged heating and ^{19}F NMR examination, which revealed large amounts of XIII, but only trace formation of the product styrenes.

Since XIII will not olefinate benzaldehyde under the same reaction conditions which XI does, the decomposition of the latter must occur via chloride ion cleavage of the carbon—mercury bond to form XVI. All chloride ion has been effectively scavenged in XIII as the trichlorozincate(II) anion, thus making the dissociative equilibrium between it and XVI impossible.



$$[((CH_3)_2N)_3\overset{+}{P}\underset{HgCl}{C}FCl]Z^- \rightleftharpoons \underset{(XVI)}{((CH_3)_2N)_3P{=}CFCl} + HgCl_2 \qquad (15)$$

(XI) $Z = Cl$, dissociation ; (XIII) $Z = ZnCl_3$, no dissociation

The unusual stability exhibited by IX, X, and in particular, XI, is not surprising in light of a report by Russian workers [40] which suggests that within a series of mercuric chloride—triphenylphosphorane quasicomplexes, the strength of the carbon—mercury bond is directly proportional to the basicity of the ylide.

Experimental

Analytical instrumentation

GLPC analyses were conducted on a Hewlett—Packard 5750B Dual Column Gas Chromatograph equipped with thermal conductivity detectors. Quantitative GLPC analyses of carbonyl olefination reaction solutions were performed by use of integrated peak area (Disc® integrator), relative to toluene or mesitylene as internal standard, after appropriate thermal conductivity factors [43] had been determined. Quantitative analyses for carbon, hydrogen, and nitrogen were performed by service personnel within this department. A Thomas—Hoover capillary melting point apparatus was utilized for the determination of corrected melting or decomposition points.

Proton NMR spectra (^{1}H NMR) were obtained by use of a Varian A-60 instrument, with positive chemical shifts reported in δ (ppm) downfield from internal tetramethylsilane (TMS). Fluorine NMR spectra (^{19}F NMR) were obtained from a Varian HA-100 spectrometer operated at 94.075 MHz. Chemical shifts are reported in ϕ^* (ppm) [44] upfield from internal trichlorofluoromethane ($CFCl_3$). Phosphorus NMR spectra (^{31}P NMR) were also recorded on a Varian HA-100 instrument, operated at 40.5 MHz, or on a Bruker 90 spectrometer equipped with Fourier transform. A phosphoric acid capillary (H_3PO_4) served as external standard; positive chemical shifts are reported in ϕ^* (ppm) upfield from this standard. All coupling constants (J) are reported in hertz (Hz).

Quantitative ^{19}F NMR analyses of reaction solutions were carried out with α,α,α-trifluorotoluene as internal standard. When the reaction was terminated, a known amount of internal standard was added, and all pertinent peaks were enlarged at constant amplitude. The NMR spectrum was then Xeroxed®, and the peaks carefully cut and weighed; further calculation revealed the amount of reactant or product present, within a determined accuracy of ±5%.

Materials and methods

All solvents and reagents were scrupulously dried prior to use as all reactions were found to be extremely moisture sensitive. DMF (MCB) was stirred with barium oxide, and after decantation was distilled at reduced pressure. Benzonitrile (MCB) was washed with aqueous sodium carbonate then water, and dried overnight with calcium chloride, followed by subsequent vacuum distillation from phosphorus pentoxide. THF (MCB) and triglyme (Ansul) were predried by stirring over sodium followed by distillation (vacuum distillation in the case of the latter) from a sodium benzophenone ketyl. All solvents were stored over 4 Å (Linde) molecular sieves in dark, septum-capped bottles under a dry nitrogen atmosphere.

Tris(dimethylamino)phosphine (VII) was prepared by the method of Organic Synthesis [45]. Zinc—copper couple was prepared from zinc dust (98%, MCB) as received, by the LeGoff procedure [46]. Other metal couples were prepared similarly by use of cadmium dust (99.5%, RO/I) and/or by substitution of mercuric acetate (Merck) for cupric acetate (Mallinckrodt) in the LeGoff method. All aldehydes and ketones were purified by standard literature procedures [47]. Most halogenated esters were prepared by modification and combination of procedures from Miller and Woolf [48] and Zawistowski [49], and methyl difluoroacetate was prepared by modification of the Organic Synthesis procedure [50]. *N*,*N*-Dimethyltrifluoroacetamide was prepared by the procedure of Bissel and Finger [51]. This compound, as well as all halogenated esters, was dried prior to reaction by distillation from phosphorus pentoxide.

All reaction glassware was dried at 120°C overnight, and assembled while still hot during a nitrogen purge. Solvents and liquid reagents were added to reaction flasks via predried, nitrogen-flushed syringes. Solid, dried reagents were handled in a glovebag under a nitrogen atmosphere, and were transferred to reaction flasks via Fieser side-arm addition tubes [52].

Preparation of quaternary phosphonium compounds

(1) (Dichlorofluoromethyl)tris(dimethylamino)phosphonium chloride (VI). Tris(dimethylamino)phosphine (44.3 g, 0.272 mol) in 75 ml dry diethyl ether was added dropwise over a 2 h period to a stirred, 0°C solution of trichlorofluoromethane (49.9 g, 0.363 mol) in 350 ml dry ether. Subsequent stirring for 2 h at 0°C overnight at room temperature was followed by isolation of the hygroscopic tan precipitate in a fritted Schlenk funnel [52] under nitrogen. Additional ether washings followed by drying with a stream of nitrogen afforded 75.5 g (0.251 mol, 92%) (VI). Its melting point was characterized by a softening at 151°C and decomposition at 218°C. (Found: C, 27.89; H, 5.92; N, 13.88%. $C_7H_{18}N_3PCl_3F$ calcd.: C, 27.97; H, 6.04; N, 13.98%.) ^1H NMR ($CDCl_3$, internal TMS): δ 3.09, d (CH_3); $J(^1H—^{31}P)$ 10.0 Hz. ^{19}F and ^{31}P NMR data are listed in Tables 6, 8 and 9.

(2) VI with zinc—copper couple; preparation of [chlorofluoro[tris(dimethylamino)phosphonio]methyl]zinc(II) chloride (IX). Generally, preparation of IX involves addition of an excess of dry zinc—copper couple to a stirred, preheated (40°C) THF solution under a nitrogen atmosphere. Incremental addition of VI occurs over the next 10 min at such a rate as to maintain the reaction solution at less than 60°C. The formation of IX is characterized by an exothermic effervescence and the formation of a homogeneous, dark brown reaction solution (VI is insoluble in THF). After additional stirring for 15 min at 40—60°C, the reaction solution is transferred under nitrogen to a fritted Schlenk funnel and filtered by positive nitrogen pressure into another reaction vessel.

Attempts to isolate IX were unsuccessful; a dark noncrystallizing oil was obtained after vacuum removal of all THF. ^{19}F and ^{31}P NMR data of IX is found in Tables 6—9. The following reactions were conduced in an attempt to form isolable derivatives of IX:

(a) IX with bromine; preparation of (bromochlorofluoromethyl)tris(dimethylamino)phosphonium bromodichlorozincate (XII). Zinc—copper couple (1.68 g, 27.8 mg at.) and VI (4.97 g, 16.5 mmol) were treated as in 2), and the resulting filtered reaction solution was cooled to 0°C. Bromine (2.94 g, 18.4 mmol) was added, and the stirred reaction solution was allowed to warm to room temperature overnight. Several THF and ether washings preceded isolation of a tan, hygroscopic salt under nitrogen which softened at 168°C and decomposed at 242°C. (Found: C, 16.09; H, 3.18; N, 7.84. $C_7H_{18}N_3PBr_2Cl_3FZn$ calcd.: C, 15.99; H, 3.45; N, 7.99%.) ^{1}H NMR (acetone-d_6, internal TMS): δ 3.07, d (CH_3); $J(^1H—^{31}P)$ 10.1 Hz. ^{19}F and ^{31}P NMR data are listed in Tables 8 and 9, respectively.

(b) IX with mercuric chloride; preparation of chloro[chlorofluoro[tris(dimethylamino)phosphonio]methyl]mercury(II) trichlorozincate (XIII). Zinc—copper couple (2.52 g, 38.6 mg at.) and VI (8.28 g, 27.5 mmol) were reacted as in 2), and mercuric chloride (8.10 g, 29.8 mmol) was then added, resulting in the immediate formation of a heavy precipitate. The reaction solution was allowed to stir overnight at room temperature, and 13.10 g (20.6 mmol; 75%) of XIII was isolated as described in 2.a.). Repeated diethyl ether washings afforded a tan, hygroscopic salt which softened at 109°C and decomposed at 167°C. (Found: C, 13.16; H, 2.97; N, 6.32. $C_7H_{18}N_3PFCl_5HgZn$ calcd.: C, 13.19; H, 2.85; N, 6.59%.) ^{1}H NMR (DMSO-d_6, TMS capillary): δ 3.34, d (CH_3); $J(^1H—^{31}P)$ 9.5 Hz. ^{19}F and ^{31}P NMR data appear in Tables 8 and 9, respectively.

(c) IX with methyl iodide; preparation of (1-chloro-1-fluoroethyl)tris(dimethylamino)phosphonium dichloroiodozincate (XIV). Zinc—copper couple (3.68 g, 56.3 mg at.) and VI (7.76 g, 25.8 mmol) were reacted as in 2), and methyl iodide (7.61 g, 53.6 mmol) was then added. After stirring overnight, a dark sludge was isolated by filtration under nitrogen, resulting in 5.60 g (11.0 mmol, 43%) crude XIV which softened at 118—128°C, with decomposition at $\simeq$133°C. Elemental analyses were not acceptable, possibly indicating the presence of residual methyl iodide. ^{1}H NMR acetone-d_6, internal TMS): δ 2.42, dd (C—CH_3); $J(^1H—^{31}P)$ 11.3 Hz; $J(^1H—^{19}F)$ 22.5 Hz; δ 3.05, d (N—CH_3); $J(^1H—^{31}P)$ 9.8 Hz. Integration of *C*-methyl/*N*-methyl protons = 1.0/6.5. ^{19}F and ^{31}P NMR data appear in Tables 8 and 9, respectively.

(d) IX with phenylmercuric chloride; preparation of [chlorofluoro[tris-(dimethylamino)phosphonio]methyl]phenylmercury(II) trichlorozincate (XV). Zinc—copper couple (3.00 g, 45.9 mg at.) and VI (8.58 g, 28.5 mmol) were reacted as in 2), and phenylmercuric chloride (8.82 g, 28.2 mmol) was then added to the homogeneous reaction solution. Phenylmercuric chloride proved to be insoluble in THF, and stirring for an additional 24 h at room temperature did not change the appearance of the contents of the reaction flask. Isolation under nitrogen afforded 5.70 g of noncrystallizing oil. ^{1}H NMR (DMSO-d_6, TMS capillary): δ 7.90, m (C_6H_5); δ 3.09, d (CH_3); $J(^1H—^{31}P)$ 9.5 Hz. ^{19}F NMR data appears in Table 8.

(3) VI with cadmium; preparation of chloro[chlorofluoro[tris(dimethylamino)-phosphonio]methyl]cadmium(II) chloride (X). VI (5.06 g, 16.8 mmol) was dissolved in 30 ml dry benzonitrile under a nitrogen atmosphere, affording a yellow, homogeneous solution. Cadmium dust (2.67 g, 23.7 mg at.) was then added, and after 20 min induction period, an exothermic discoloration to dark green, then dark brown occurred. The reaction temperature was quickly cooled to 60°C, and subsequent ^{19}F NMR analysis revealed the presence of traces of residual VI, and large amounts of X (see Table 7 for spectral data). There were also small amounts of $CFCl_2H$ (ϕ^* 80.1; d; $J(^{19}F—^1H)$ 52 Hz [53]), $((CH_3)_2N)_3$-$PFCl$ (ϕ^* 84.8, d; $J(^{19}F—^{31}P)$ 958 Hz [54,55]), and $[((CH_3)_2N)_3\overset{+}{P}CFClH]X^-$ (ϕ^* 151.2, dd; $J(^{19}F—^{31}P)$ 68 Hz; $J(^{19}F—^1H)$ 42 Hz [30]). Subsequent addition of mercuric chloride (7.22 g, 26.6 mol) and ^{19}F NMR reanalysis revealed dis-

appearance of the signal attributable to X, and appearance of signals characteristic of a mercurated salt, as detailed in eq. 13: $[((CH_3)_2N)_2\overset{+}{P}CFCl(HgCl)][CdCl_3]^-$, ϕ^* 122.4, d with satellite peaks; $J(^{19}F—^{31}P)$ 68 Hz; $J(^{19}F—^{199}Hg)$ 700 Hz.

(4) VI with mercury; preparation of chloro[chlorofluoro[tris(dimethylamino)-phosphonio]methyl]mercury(II) chloride (XI). VI (3.78 g, 12.6 mmol) was added to 10 ml dry benzonitrile under a nitrogen atmosphere followed by addition of mercury (1.0 ml, 67.8 mg-at.). Heating at 60°C for 83 hours was followed by ^{19}F NMR analysis which revealed primarily XI (see Table 7 for ^{19}F NMR data), as well as traces of VI, $((CH_3)_2N)_3PFCl$, and $[((CH_3)_2N)_3\overset{+}{P}CFClH]$-$X^-$ (see 3) above). Addition of α,α,α-trifluorotoluene as ^{19}F NMR internal standard was followed by benzaldehyde (1.07 g, 10.1 mmol). Subsequent reaction for 4 h at 60°C and ^{19}F NMR reanalysis revealed 9.1 mmol (73%) *E*- and *Z*-β-chloro-β-fluorostyrene in a ratio of 49/51 [20].

Preparation of chlorofluoromethylene olefins

All olefination reactions were conducted with an excess of dechlorination agent and VI relative to the carbonyl component; olefin yields are based on the carbonyl component. The olefins listed in Tables 1—3 were unambiguously identified by comparison of their spectroscopic properties relative to authentic samples [20]. The vinyl ethers reported in Table 4 were identified by comparison of their ^{19}F NMR spectra to those reported for *cis*- and *trans*-3-methoxyperfluoro-2-pentene [25]. The ^{19}F NMR data for those vinyl ethers of Table 4 is listed in Table 5.

(1) Metal and solvent survey. The following procedure is representative. Acetophenone (1.34 g, 11.1 mmol) and zinc—copper couple (2.89 g, 44.3 mg at.) were added to 50 ml dry triglyme under a nitrogen atmosphere. Incremental addition of VI (4.22 g, 14.1 mmol) over ten minutes to the 40°C reaction solution afforded an exothermic discoloration of the contents of the reaction flask. Stirring for an additional 5 h at 60°C, followed by GLPC analysis with mesitylene as internal standard, revealed 8.0 mmol (72%) *E*- and *Z*-1-chloro-1-fluoro-2-phenylpropene in a 50/50 ratio.

(2) Carbonyl survey. (a) Benzaldehyde. The following procedure is representative. Benzaldehyde (1.04 g, 9.8 mmol) was added to a stirred, 45°C slurry of zinc-copper couple (3.63 g, 48.1 mg at.) in 50 ml dry THF under a nitrogen atmosphere. VI (3.94 g, 10.9 mmol) was added over a 10 min period, causing the color of the contents of the reaction flask to turn a dark brown. Reaction for an additional hour at 60°C preceded GLPC analysis with mesitylene as internal standard, revealing 9.8 mmol (100%) *E*- and *Z*-β-chloro-β-fluorostyrene in a ratio of 47/53.

(b) Isopropyl trifluoroacetate. The following procedure is representative. Isopropyl trifluoroacetate (2.24 g, 14.4 mmol) was reacted with zinc—copper couple (2.27 g, 34.8 mg at.) and VI (5.75 g, 19.1 mmol) in 40 ml dry triglyme under a nitrogen atmosphere as described in 2.a.). After 19.5 h at 60°C, α,α,α-trifluorotoluene was added as ^{19}F NMR internal standard; subsequent ^{19}F NMR analysis revealed 7.3 mmol (51%) *E*- and *Z*-1-chloro-2-isopropoxyperfluoropropene in a ratio of <0.1. GLPC analysis with toluene as internal standard indicated 6.8 mmol (47%) unreacted isopropyl trifluoroacetate.

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