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**Fluorinated Organometallics: Vinyl, Alkynyl, Allyl, Benzyl,
Propargyl and Aryl
Fluorinated Organometallic Reagents in Organic Synthesis****Donald J. Burton*, Zhen-Yu Yang†, and Peter A. Morken**

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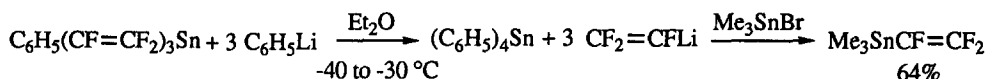
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Fluorinated organometallic reagents provide a general method for the introduction of fluorine into organic molecules. However, due to the limited thermal stability of many of these fluorinated organometallic reagents, their chemistry is much less developed than that of their hydrocarbon analogs. Nevertheless, in the last several years dramatic progress has been made in the preparation and application of fluorovinyl tin and zinc reagents, which exhibit superior thermal stability. Concomitant advances in the utility of several stable alkynyl and aryl fluorinated organometallics have been reported. We recently reviewed the chemistry of perfluoroalkyl and functionalized perfluoroalkyl organometallic reagents.¹ This report will focus on the preparation and synthetic utility of reagents including vinyl, alkynyl, allyl, benzyl, propargyl and aryl fluorinated organometallic compounds. Literature prior to May, 1993 has been included. A previous review detailed the chemistry of pentafluorophenyl organometallics, and most of this material will not be included here, except for historical perspective.² A corresponding review on fluorinated alkynes describes fluorinated alkynyl organometallics.³ Additionally, the aryl organometallic section will be limited to pentafluorophenyl organometallics, and thus reagents such as 2,4,6-(CF₃)₃C₆H₂Li⁴,⁵ will not be discussed. Organometallic reagents that have not been reported to exhibit synthetic utility generally were not included, and we apologize to those authors.

We recognize that magnesium, zinc, and cadmium reagents exist in solution as a mixture of mono and bis reagents, as related by the Schlenk equilibrium. In this report we usually denote the organometallic reagents as RMX, where X can be a halide (mono reagent) or R (bis reagent). The reader should also be aware that the presence of an F in a ring implies that all unmarked positions are attached to fluorine atoms.

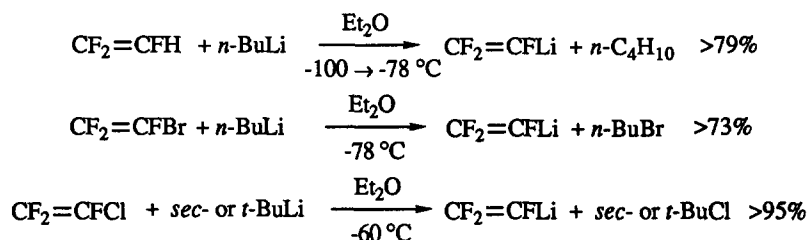
1. Fluorovinyl Lithium Reagents

Early efforts to prepare trifluorovinyl lithium in solution from the reaction of trifluorovinyl halides with metallic lithium failed,⁶ a result similar to the failure⁷ of iodotrifluoromethane and lithium metal to give trifluoromethyl lithium reagent. Seyferth and co-workers first generated trifluorovinyl lithium in solution from the reaction of phenyllithium and phenyltris(trifluorovinyl)tin (3:1 molar ratio) in ether between -40 to -30 °C.⁸ This vinyl lithium could be trapped by trimethyltin bromide, triethyltin chloride and trimethylsilyl bromide to afford trimethyltrifluorovinyltin, triethyltrifluorovinyltin and trimethyltrifluorovinylsilane in 64%, 40% and 45% yields, respectively. A similar exchange reaction of *n*-butyllithium and *n*-butyltris(trifluorovinyl)tin in pentane also gave the corresponding trifluorovinyl lithium reagent in 45-50% yields.

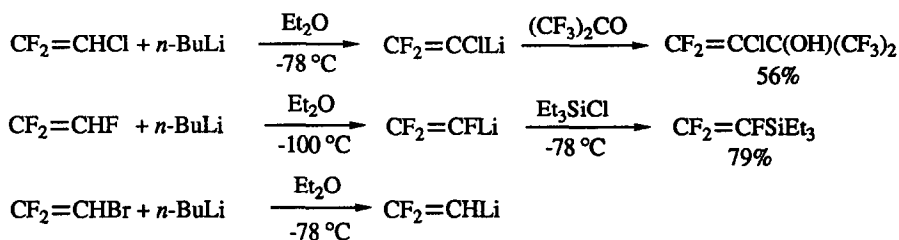


During the last three decades, trifluorovinyl lithium has been most conveniently prepared by lithium-halogen⁹ and lithium-hydrogen¹⁰ exchange reactions. The thermal stability of trifluorovinyl lithium was found to be dependent upon the solvent. The lowest thermal stability is exhibited in THF. Treatment of bromotrifluoroethylene with alkyl lithium reagents such as *n*-butyllithium or methyl lithium gave the trifluorovinyl lithium in good yields.⁹ The exchange reaction was usually carried out in ether at -78 °C. However, reaction of chlorotrifluoroethylene with *n*-butyllithium in ether at -70 °C gave the addition-elimination product (1,2-difluoro-1-chloro-1-hexene) and butyl chloride. No trifluorovinyl lithium was

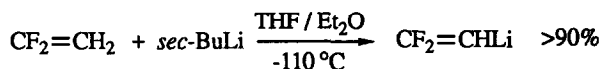
formed.^{11, 12} Although the corresponding lithium reagent could be obtained when a mixture of THF, ether and pentane was utilized as solvent, it was necessary to conduct the reaction at a temperature of $-135\text{ }^{\circ}\text{C}$ to avoid decomposition of trifluorovinyl lithium in the presence of THF.¹¹ An improved procedure has been developed to prepare trifluorovinyl lithium from the less expensive trifluorovinyl chloride under more accessible conditions. Normant found that the reaction of trifluorovinyl chloride with *sec*- or *t*-butyllithium in ether at $-60\text{ }^{\circ}\text{C}$ produced trifluorovinyl lithium in almost quantitative yield.¹³ This protocol provides an inexpensive and high yield method for the generation of trifluorovinyl lithium under relatively mild conditions.



The attempted halogen-lithium exchange of 2,2-difluoro-1-chloroethylene with *n*-butyllithium in ether at $-78\text{ }^{\circ}\text{C}$ gave no 2,2-difluoroethenyllithium. Lithium-hydrogen exchange occurred to give 2,2-difluoro-1-chloroethenyllithium.¹⁴ Similar exchange reaction of trifluoroethylene with *n*-butyllithium afforded trifluorovinyl lithium.¹⁴ However, with 2,2-difluoro-1-bromoethylene, lithium-bromine exchange was the favored exchange reaction and 2,2-difluoroethenyllithium was formed.¹⁴ These findings indicated that the order of exchange reactivity was $\text{Li-Br} > \text{Li-H} > \text{Li-Cl}$.

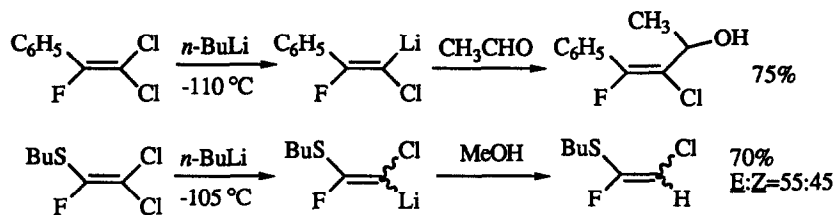


Metallation of 1,1-difluoroethene was accomplished by treatment with *sec*-butyllithium in THF and ether (80/20) at $-110\text{ }^{\circ}\text{C}$.^{15, 16} Side reactions were observed when *n*-BuLi was utilized for the lithium-hydrogen exchange reaction.

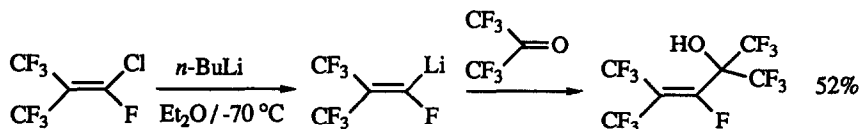


1,2-Difluorodichloroethylene and 2,2-difluorodichloroethylene¹⁷ were treated with *n*-butyllithium at -100 to $-110\text{ }^{\circ}\text{C}$ in ether / THF to give the corresponding lithium reagents, which reacted with carbonyl substrates to produce carbinols. Metallation of 2-fluoro-2-phenyldichloroethylene with *n*-butyllithium in ether gave predominately one isomeric lithium reagent, which could be trapped with carbon dioxide or aldehydes to afford

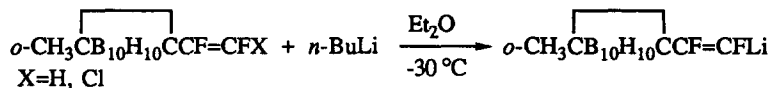
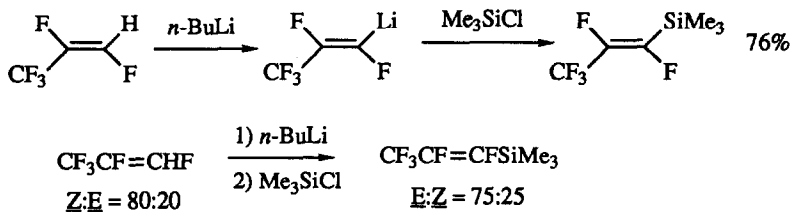
the carboxylic acid and allylic alcohols with *Z*-geometry, respectively.¹⁸ In contrast, the vinyl lithium formed from $\text{BuSCF}=\text{CCl}_2$ is not stereoselective.¹⁸

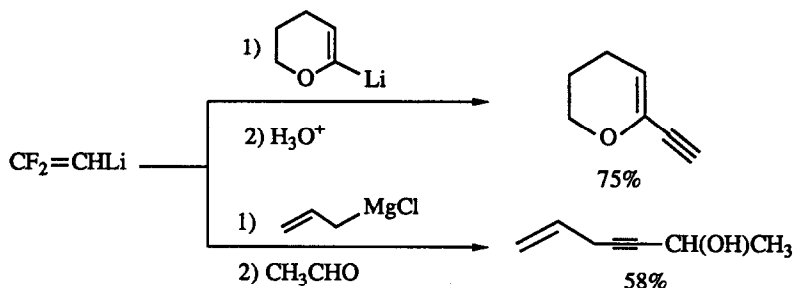


Perfluoro-1-chloro-2-methylpropene underwent exchange reaction with *n*-butyllithium to form the corresponding vinyl lithium. Subsequent reaction with hexafluoroacetone afforded the perfluorocarbino. The same vinyl lithium was not formed in appreciable amounts by attempted metallation of $(\text{CF}_3)_2\text{C}=\text{CHF}$ with *n*-BuLi in ether at -78°C . The main product observed arose from an addition/elimination reaction with the alkyl lithium reagent.

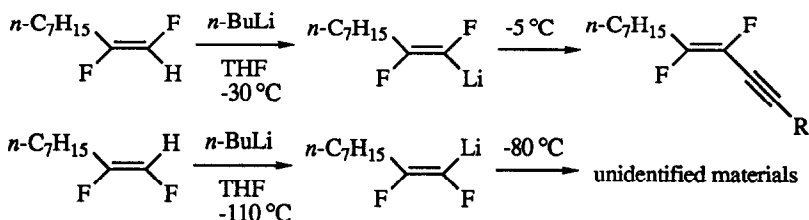


Other polyfluoroalkenyl lithium reagents could be synthesized by similar methods. An early report described that only *Z*-perfluoropropenyl lithium was formed after the treatment of a 1:1 mixture of *Z*- and *E*- $\text{CF}_3\text{CF}=\text{CFH}$ with *n*-butyllithium in ether at -78°C .²⁰ Tarrant and co-workers proposed that the *E*-lithium reagent isomerized readily to the *Z*-lithium reagent. However, reinvestigation by Burton and co-workers indicated that the rearrangement of *E*- $\text{CF}_3\text{CF}=\text{CFLi}$ to *Z*- $\text{CF}_3\text{CF}=\text{CFLi}$ did not occur.²¹ Upon metallation of pure *E*- $\text{CF}_3\text{CF}=\text{CFH}$ or an 80:20 mixture of *Z*- and *E*- $\text{CF}_3\text{CF}=\text{CFH}$ with *n*-butyllithium at -78°C , the stereochemical integrity of the lithium reagents was completely preserved. *E*- and *Z*-1,2-difluoroalkenes¹³ as well as *trans*-fluorovinylcarboranes also gave the corresponding lithium reagents stereospecifically.²²

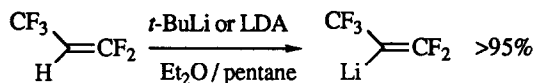




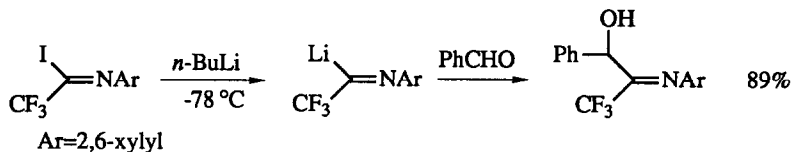
E-Difluorovinyl lithium reagents are more stable than their *Z*-analogs. *E*-Difluorononyllithium could be prepared at $-30\text{ }^\circ\text{C}$ in THF and decomposed above $-5\text{ }^\circ\text{C}$ to give a difluoroenyne.^{13, 27} In contrast, *Z*-difluorononyllithium was observed in a mixture of ether and THF at $-110\text{ }^\circ\text{C}$, but decomposed to unidentified materials upon warming to $-80\text{ }^\circ\text{C}$.



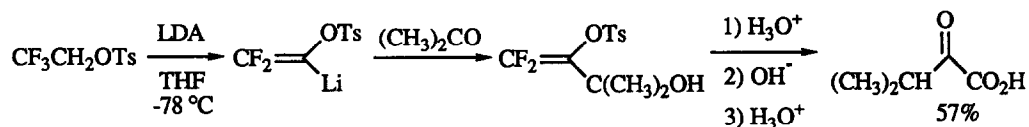
An internal fluorovinyl lithium reagent has been prepared by a similar lithium-hydrogen exchange reaction. Treatment of 2-hydropentafluoropropene with either *t*-butyllithium or LDA in ether/pentane at $-78\text{ }^\circ\text{C}$ gave $\text{CF}_3\text{CLi}=\text{CF}_2$ in high yield.²⁸ Poorer yields of the lithium reagent were obtained with *n*-butyllithium in ether/pentane or LDA in pentane.



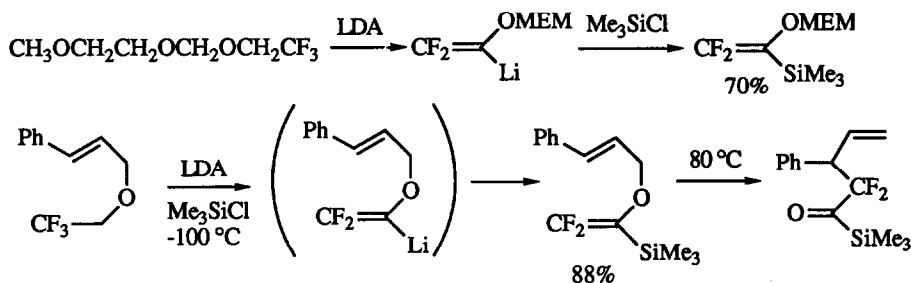
N-Aryl trifluoroacetimidoyl lithiums²⁹ have been prepared by low temperature lithium-halogen exchange reaction with *N*-aryl trifluoroacetimidoyl iodides.³⁰ These trifluoroacetyl carbanion equivalents were readily trapped by electrophiles, including acid chlorides, aldehydes, ketones, trimethylsilyl chloride, ethyl chloroformate and *N,N*-dimethylformamide.



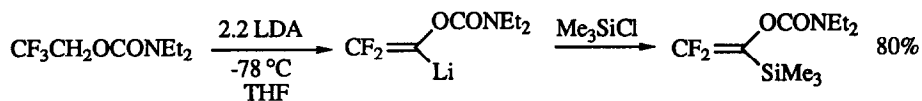
Recently, α -oxygen-substituted difluorovinyl lithium reagents have received attention since they could be readily prepared under mild conditions and were demonstrated to be versatile and useful building blocks for the synthesis of organofluorine compounds.³¹ Nakai and co-workers first prepared 2,2-difluoro-1-tosyloxyvinyl lithium from the reaction of 2,2,2-trifluoroethyl tosylate with two equivalents of LDA in THF at $-78\text{ }^\circ\text{C}$. This reagent reacted with carbonyl substrates, to give an adduct which after hydrolysis afforded α -keto acids in good yields.³²



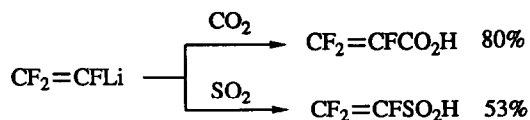
2,2-Difluoro-1-alkoxylithiums could also be prepared by a one-pot dehydrofluorination and exchange reaction, followed by quenching with trimethylsilyl chloride.^{33, 34, 35}



Other examples of α -oxygen-substituted difluorovinyl lithium reagents include a carbamate, generated by treatment of a 2,2,2-trifluoroethyl carbamate with 2.2 equivalents of LDA at $-78\text{ }^\circ\text{C}$ in THF.^{36, 37}

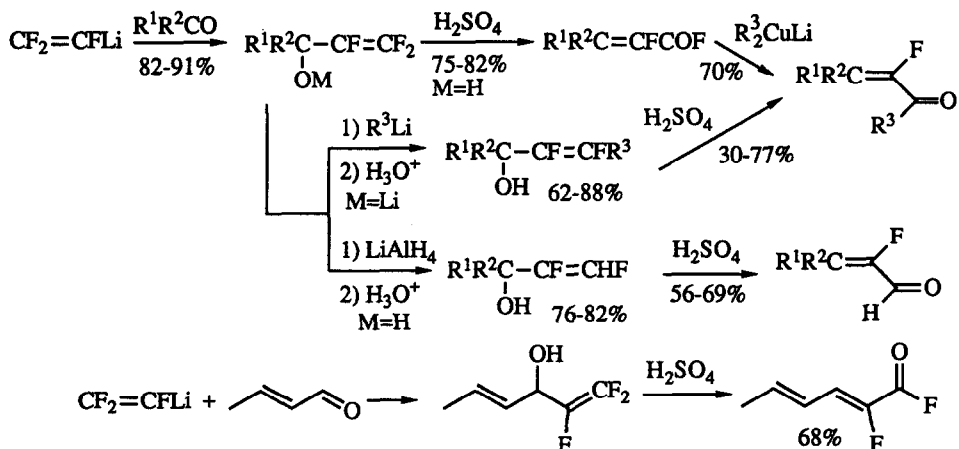


Fluorinated vinyl lithium reagents readily react with a variety of electrophiles. Trifluorovinyl lithium reacts with proton, halogen, trialkylsilyl chloride, trialkyltin chloride, methyl iodide, carbon dioxide and sulfur dioxide electrophiles to form trifluorovinylated products.^{8, 12, 13}

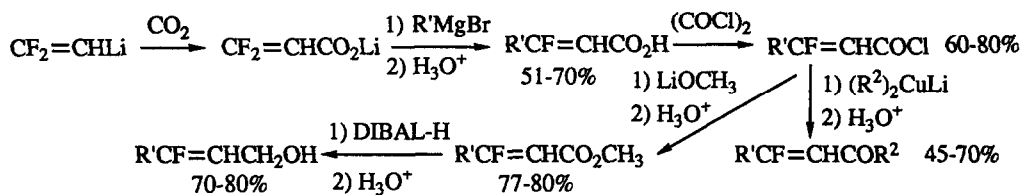


Trifluorovinyl lithium also reacts with aldehydes or ketones to give the corresponding carbinols, which can undergo acid- or thermally-promoted rearrangement to give α -fluoro- α,β -unsaturated acid fluorides.¹¹

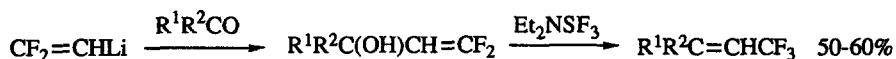
Application of this methodology has led to the preparation of fluorinated analogs of the aldehyde portion of the boll weevil pheromone.³⁸ Reaction of the acid fluorides with lithium dialkylcuprates has provided a new approach to α -fluoro- α,β -unsaturated ketones which are difficult to obtain by other methods.¹¹ Treatment of the carbinols with alkyllithium or lithium aluminum hydride gives α,β -difluoroallylic alcohols, which can be hydrolyzed in sulfuric acid to produce α -fluoro- α,β -unsaturated ketones and aldehydes, respectively.³⁹ With α,β -unsaturated aldehydes, trifluorovinyl lithium gave only the 1,2-addition product, which also readily underwent rearrangement upon hydrolysis to give the acid fluoride.¹¹

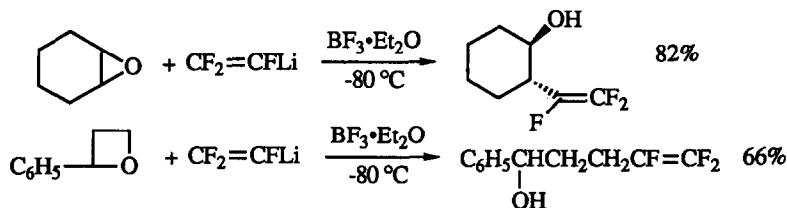


2,2-Difluorovinyl lithium reacts with carbon dioxide, followed by acid to give the corresponding acrylic acid derivative, which is difficult to isolate due to the ease of hydrolysis at room temperature. Thus, functionalization reactions are carried out on the lithium difluoroacrylate salt. Reaction of this salt with organomagnesium halides affords β -fluoro- α,β -unsaturated acids. Further reactions of the acid products with oxalyl chloride and nucleophiles leads to β -fluoro- α,β -unsaturated ketones, esters and alcohols.⁴⁰

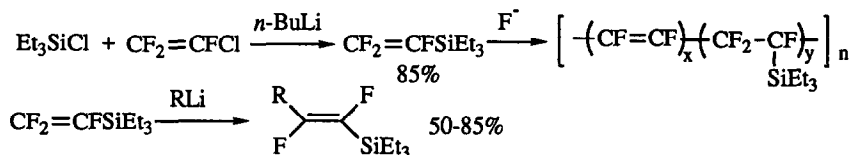


Capture of 2,2-difluorovinyl lithium with aldehydes yielded the expected alcohols. Treatment of the alcohols with DAST gave the rearranged *E*-alkenes.⁴¹

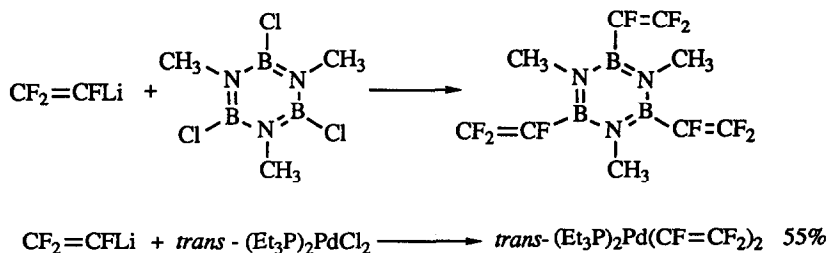




Tarrant generated trifluorovinyltriethylsilane in 79% yield from the reaction of trifluorovinyl lithium and triethylsilyl chloride.¹⁴ Trifluorovinyl alkoxy silanes and disiloxanes were similarly prepared.⁴⁴ A somewhat better yield was obtained by Hiyama using Barbier conditions at low temperature. He also generated a number of mono-, bis- and tris(trifluorovinyl)organosilanes.⁴⁵ Trifluorovinylsilane was polymerized *via* fluoride ion catalysis to give a fluorinated metallic polymer with conductivity of 10^{-9} to $10^{-10} \Omega^{-1}\text{cm}^{-1}$. Treatment of the trifluorovinylsilane with organolithium reagents stereospecifically formed *Z*-1,2-difluoroalkenylsilanes, which are versatile fluorinated synthons.⁴⁶ Chlorodifluorovinylsilanes were prepared *via* the analogous reaction of $\text{CF}_2=\text{CClLi}$ with chlorotrimethylsilane.⁴⁷

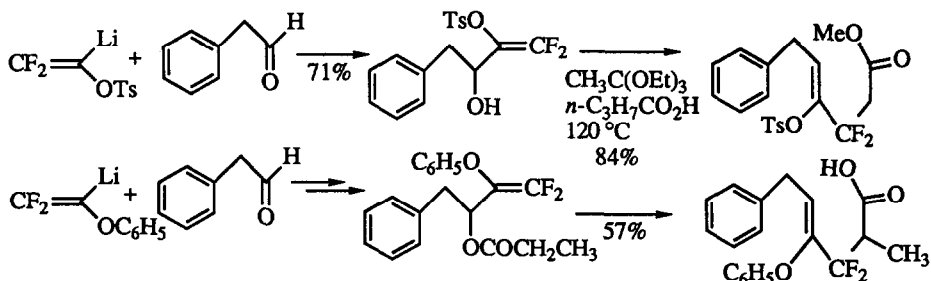


Fluorovinyl lithium reagents have been widely utilized for the preparation of fluorovinyl main group element and metallic compounds. Reactions with β -chloro substituted borazines⁴⁸ and trialkyltin,⁸ mercury,⁹ nickel,⁴⁹ palladium⁴⁹ and platinum⁴⁹ halides gave the fluorovinylated products. Trifluorovinyl derivatives of several elements have been reviewed by Russian workers.⁵⁰

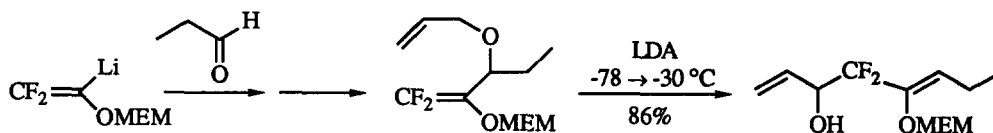


Reaction of 2,2-difluoro-1-tosyloxyvinyl lithium with carbonyl substrates gave fluorinated allyl alcohols, which underwent orthoacetate Claisen rearrangements to provide useful difluoro functionalized esters or acids. 2,2-Difluoro-1-phenyloxyvinyl lithium was also trapped with phenylacetaldehyde to yield an allylic alcohol.

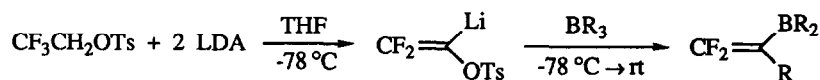
After esterification, the alcohol underwent an Ireland enolate Claisen reaction and hydrolysis to give a β,β -difluorocarboxylic acid.³⁴



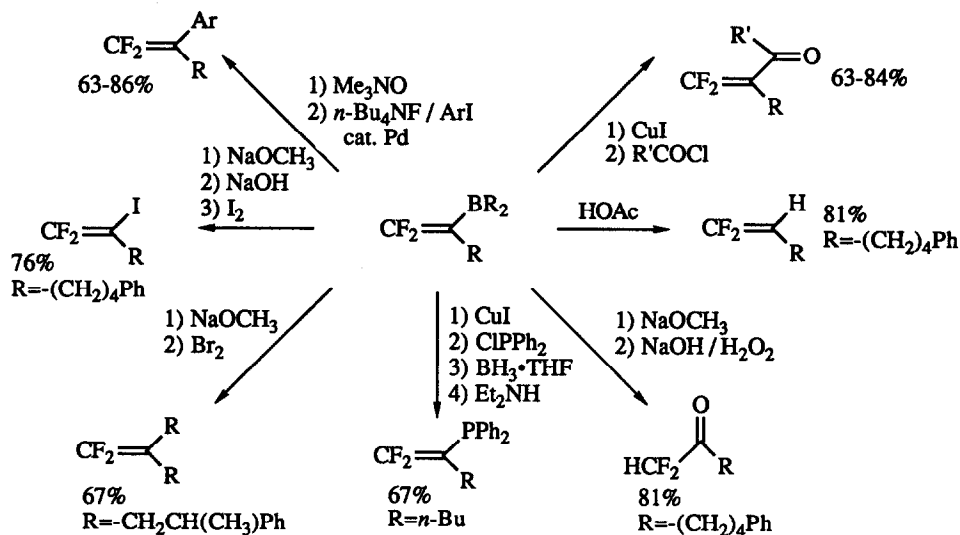
Trapping of 2,2-difluoro-1-(MEM-O)vinyl lithium with propanal gave an alcohol, which after conversion to an allyl ether, readily rearranged at -30°C in THF.³³



Reaction of 2,2-difluoro-1-tosyloxyvinyl lithium with trialkylboranes gave 2,2-difluorovinylboranes, which underwent a variety of interesting functionalization reactions.⁵¹ Treatment of the

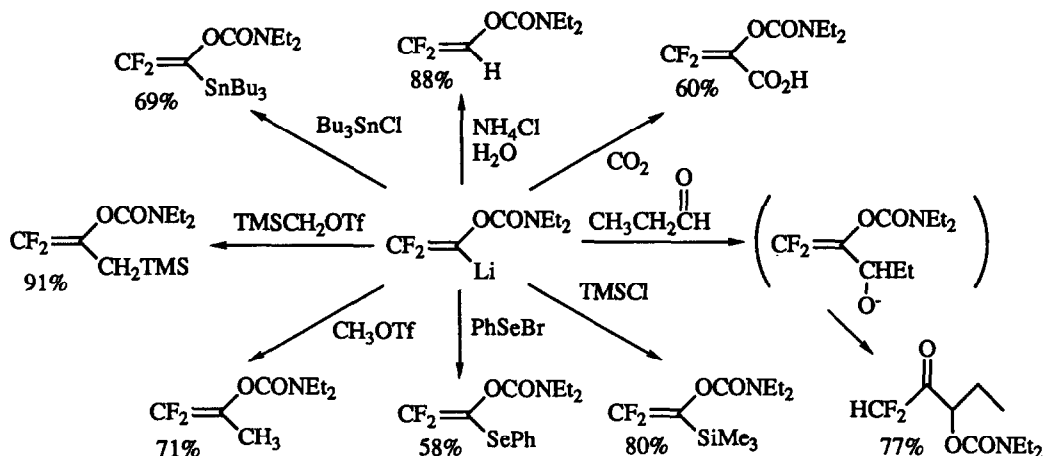


2,2-difluorovinylboranes with acid or with NaOMe and H_2O_2 / NaOH gave 1,1-difluoroalkenes and α,α -



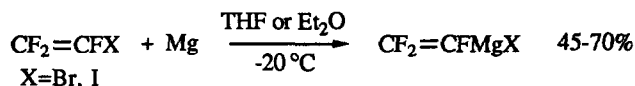
difluoro ketones, respectively.^{51, 52} When the difluorovinylborane was reacted with NaOMe followed by bromine, the expected vinyl bromide was not formed. Instead, a symmetrically disubstituted 1,1-difluoro-1-alkene was obtained.⁵³ These results are in contrast to brominolysis of non-fluorinated alkenyldialkylboranes, which give the corresponding alkenyl bromides. However, iodinolysis of the vinylboranes with iodine under basic conditions gave the expected alkenyl iodides in 56-76% yields.⁵³ The difluorovinylborane coupled with aryl iodides in the presence of a catalytic amount of $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2$ after treatment with trimethylamine *N*-oxide and tetrabutylammonium fluoride.⁵⁴ The difluorovinylborane also coupled with aryl iodides in the presence of CuI and palladium catalyst to afford improved (83-94%) yields of the 1,1-difluoroalkenes.⁵⁵ Coupled products of difluorovinylborane with acid chlorides⁵⁶ or chlorodiphenylphosphine⁵⁷ were obtained in the presence of cuprous iodide.

The difluorovinyl lithium reagent derived from 2,2,2-trifluoroethyl carbamate and LDA has been trapped by a number of electrophiles, including trimethylsilyl chloride, phenylselenenyl bromide, methyl triflate, trimethylsilylmethyl trifluoromethanesulfonate, tributyltin chloride, ammonium chloride, carbon dioxide, and propanal.^{36, 37} In the latter instance, the initially formed alkoxide adduct is observed immediately after addition of propanal, but a rearrangement to the α,α -difluoromethyl ketone quickly occurs. Attempted trapping of the lithium carbamate intermediate with methyl iodide was not successful.



2. Fluorovinyl Magnesium Reagents

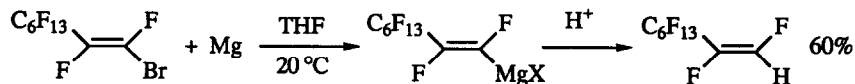
Early reports for the preparation of fluorovinyl Grignard reagents focused on trifluorovinylmagnesium halides.⁵⁰ Reaction of trifluorovinyl iodide with magnesium in ether under reflux gave trifluorovinylmagnesium iodide, albeit in low yield.⁵⁸ The low yield was caused by decomposition of the Grignard reagent at this temperature. When the reaction was carried out at $-20\text{ }^{\circ}\text{C}$, trifluorovinylmagnesium iodide was obtained in 70% yield.⁵⁹ Trifluorovinyl bromide also smoothly reacted with magnesium to give the trifluorovinylmagnesium bromide in THF at $-20\text{ }^{\circ}\text{C}$.



Exchange reactions involving halogen-magnesium^{60, 61} or tin-magnesium⁶² provide alternative routes to fluorovinylmagnesium halides. Treatment of trifluorovinyl iodide or triphenyltrifluorovinyltin with phenylmagnesium bromide gave trifluorovinylmagnesium halide.^{60, 62}

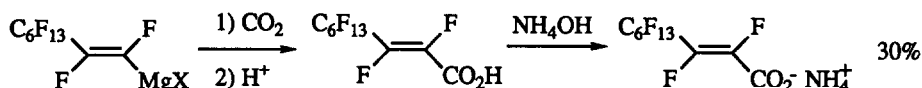


Z-Perfluoroalkenyl halides became readily available from either decomposition of perfluoroalkylmagnesium halides in ether or pentane^{63, 64, 65, 66, 67} or iodination of perfluoroalkenylphosphonium salts.⁶⁸ With these precursors in hand, perfluoroalkenylmagnesium halides were prepared from them by either direct reaction with magnesium or exchange reaction with organomagnesium halides.⁶⁹

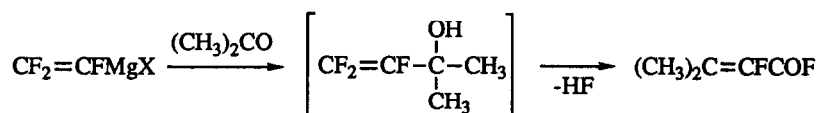


Although they are more stable than the corresponding lithium reagents, the fluorovinyl magnesium reagents are still thermally labile. Most fluorovinylmagnesium halides can be prepared at -20 to 5°C . Perfluorooctenylmagnesium bromide has been obtained in THF solution at room temperature. A detailed investigation of the stability of fluorovinyl Grignard reagents has not been reported.

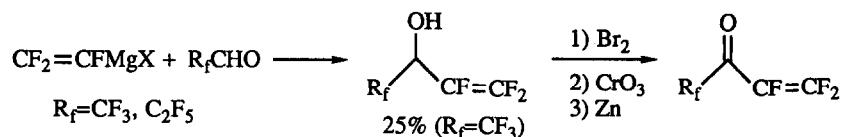
Perfluoroalkenylmagnesium halides react with a variety of electrophiles to give perfluoroalkenylated products. They have been treated with carbon dioxide to afford the perfluoroalkenoic acids.⁶⁹



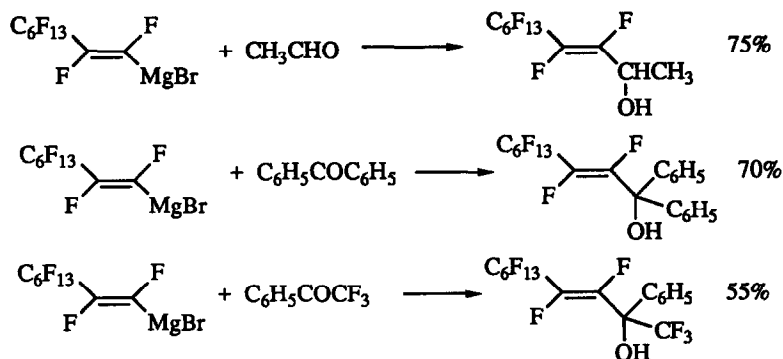
Trifluorovinylmagnesium halides attack the carbonyl group of ketones and aldehydes to give carbinols, which spontaneously rearrange to the fluorinated α,β -unsaturated acid fluorides.^{10, 70} However, a trifluorovinyl steroid was prepared in 49% yield from the reaction of the estrone 3-methyl ether with trifluorovinylmagnesium bromide. In this reaction no rearrangement product was observed.⁷¹



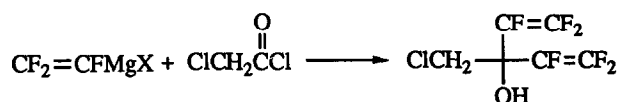
Reaction of trifluorovinylmagnesium bromide with fluorinated aldehydes or ketones led to secondary and tertiary alcohols, which were stable and isolable in pure form.¹⁰ The secondary alcohols could be transformed, albeit in low yield, to perfluoro- α,β -unsaturated ketones by a bromination, oxidation and debromination sequence.⁷²



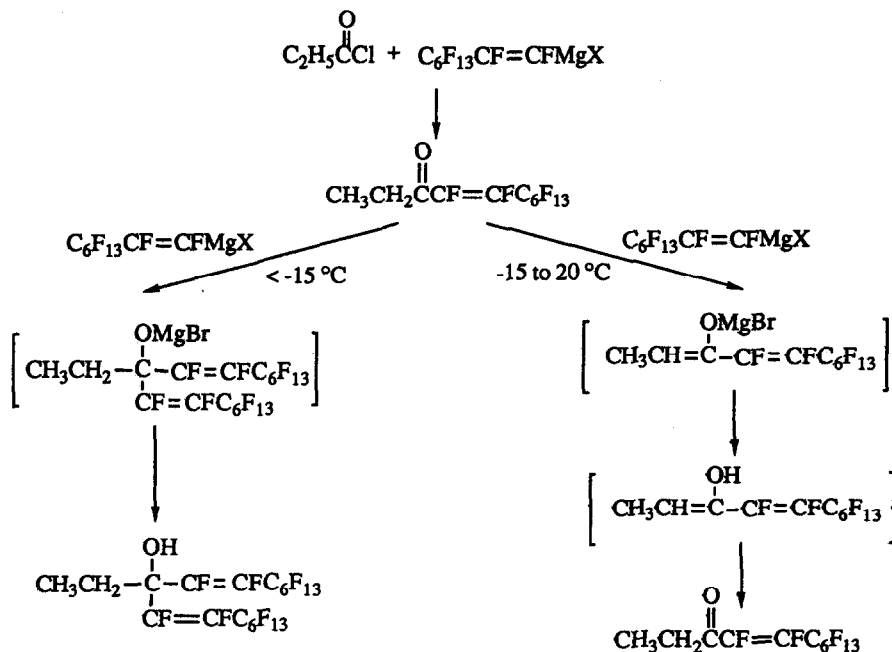
In contrast to the reactions of trifluorovinylmagnesium halides, perfluorooctenylated alcohols were readily isolated in good yields from reaction of perfluorooctenylmagnesium bromide with both non-fluorinated and fluorinated carbonyl substrates.⁷³



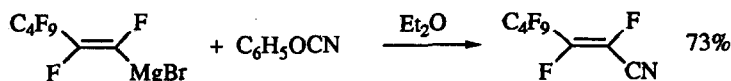
Acid chlorides have also been employed as reactants. Reaction of trifluorovinyl magnesium bromide with chloroacetyl chloride gave di(trifluorovinyl)chloromethyl alcohol, which was stable and was isolated.⁵⁰



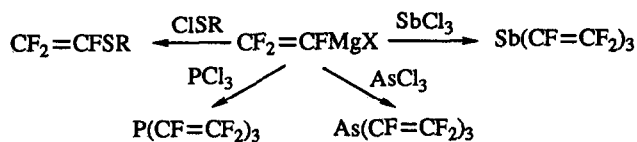
Commeyras and co-workers reported the reaction of perfluorooctenylmagnesium bromide with aliphatic acid chlorides.⁷⁴ These reactions resulted in the formation of a mixture of the desired ketone and a tertiary alcohol. The product distribution was dependent upon the reaction conditions and the acid chloride. With acetyl chloride, ketone formation was favored at low reaction temperatures (-15 to 0 °C), while with propionyl chloride or isobutyryl chloride, ketone formation was favored at higher reaction temperatures (20-35 °C) while the formation of carbinol took place at lower temperatures. This unusual temperature dependence was rationalized by the proposal that the ethyl and isopropyl ketones preferentially undergo enolization with a second equivalent of Grignard reagent, which behaves as a base at elevated temperatures. The resultant enolates could not be further attacked by Grignard reagent to form the tertiary alcohols. At lower temperatures, enolization of the ketone does not occur, and excess Grignard reagent reacts with the carbonyl group of the ketone to form the tertiary alcohols. However, close examination of the data given by Commeyras raises serious questions as to the validity of these proposals. Commeyras stated that reaction of this Grignard reagent with propionyl or isobutyryl chlorides, quenched after 15 hours at 0 °C, gave predominantly tertiary alcohols. However, the preparation of ethyl and isopropyl ketones, in which the acid chlorides were added at 0 °C followed by warming to reflux after 15 hours, gave similar results to preparations in which the acid chlorides were added at 20-35 °C. Thus, it is unclear how enolate formation at elevated temperatures could prevent tertiary alcohol formation if the tertiary alcohols were already formed at low temperatures. Another interpretation of the results is that tertiary alcohols were formed in all cases, but with bulkier alkyl groups the magnesium salts of the alcohols reverted back to the ketones upon warming.



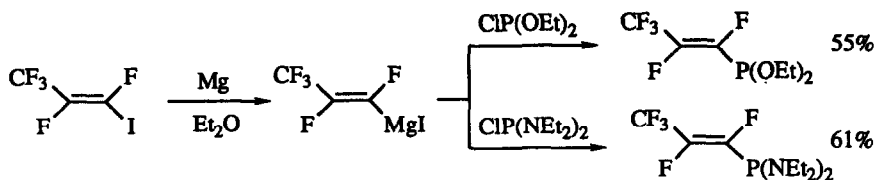
Wakselman reported that perfluorohexenylmagnesium bromide reacted with phenyl cyanate in ether to give the corresponding vinyl nitrile in 73% yield.⁷⁵



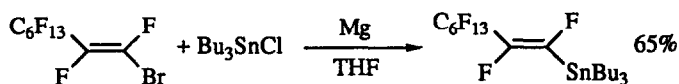
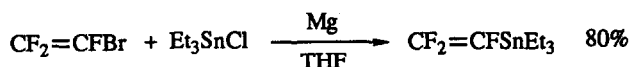
Trifluorovinylmagnesium halides are efficient trifluorovinylating reagents for the preparation of trifluorovinylated metalloids compounds.⁵⁰ Treatment of trifluorovinylmagnesium bromide with alkylsulfenyl chloride gave the trifluorovinyl alkyl sulfides in excellent yields. Trifluorovinylphosphine,⁵⁰ arsine,⁷⁶ stibine⁵⁰ and borane⁷⁶ compounds could be similarly prepared by the reaction of trifluorovinyl Grignard reagents with the corresponding halides.



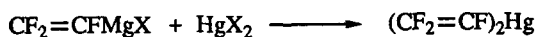
Rosenthaler treated *Z*-pentafluoropropenylmagnesium iodide with diethyl chlorophosphate or bis(diethylamino)chlorophosphine to give *Z*-pentafluoropropenylated phosphites and phosphines.⁷⁷



Perfluoroalkenylmagnesium halides were also utilized to prepare perfluoroalkenylated metallic compounds. Although pregenerated perfluoroalkenyl Grignard reagents reacted with organotin halides to give the corresponding perfluoroalkenyltin compounds, Barbier-type conditions were found to be more efficient.⁷⁸ Treatment of bromotrifluoroethylene with magnesium in the presence of organotin chloride, dichloride or tetrachloride afforded trifluorovinyltin, bis(trifluorovinyl)tin and tetrakis(trifluorovinyl)tin, respectively.^{76,79,80,81}

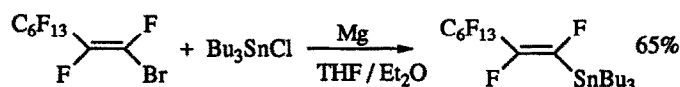
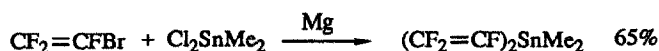


Similarly, perfluoroalkenylmercury compounds could be prepared from the alkenyl Grignard reagents.^{50, 78}

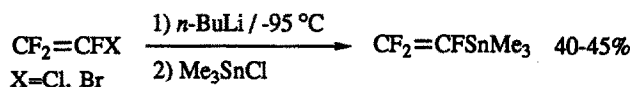


3. Fluorovinyl Tin Reagents

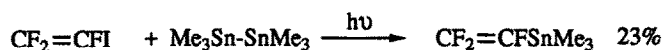
Reaction of perfluoroalkenyl Grignard reagents or lithium reagents with organotin halides provides the most general method for the preparation of perfluoroalkenyltin compounds.^{79, 80, 81} Treatment of pregenerated trifluorovinylmagnesium halides with trialkyltin chlorides or bromides gave trifluorovinyltin derivatives. With diorganotin dihalides or organotin trichlorides, the vinyl lithium or Grignard reagents afforded bis(trifluorovinyl)diorganotin and tris(trifluorovinyl)organotin, respectively. In general, the best yields were obtained in the trifluorovinylation of triorganotin halides, the poorest in the complete trifluorovinylation of organotin trihalides. When Barbier conditions were used, the yields of vinyltin compounds were improved.⁷⁸ This procedure could be employed to prepare a variety of perfluoroalkenyltin derivatives.



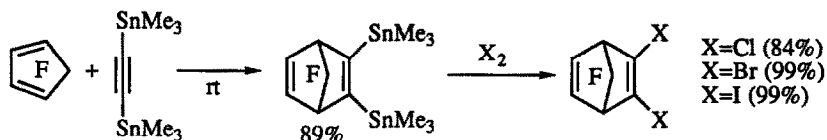
Vinyl lithium reagents could also be trapped with a tin electrophile to afford the vinyltin reagents.⁸



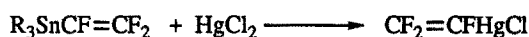
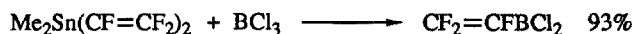
Trifluorovinyltrimethyltin was also prepared by irradiation of trifluorovinyl iodide and hexamethylditin.⁸²



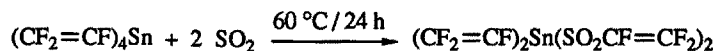
Haszeldine reported the Diels-Alder reaction of perfluorocyclopentadiene with bis(trimethylstannyl)acetylene at room temperature to give the corresponding vinyldistannane in 89% yield.⁸³ Cleavage of the trimethylstannane moieties was readily effected with halogens.



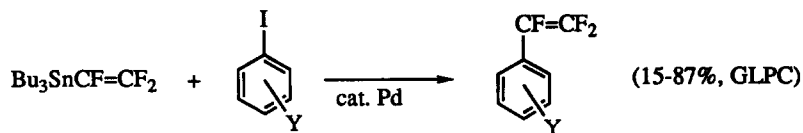
The trifluorovinyltin compounds are very reactive and less stable than their non-fluorinated counterparts. They are sensitive to oxygen, acids, bases, and also react with electrophiles such as boron trichloride⁸⁴ to afford mono-, bis-, and tris(trifluorovinyl)boron derivatives. Exchange reaction of the vinyltin reagent with mercury chloride in ether gave the vinylmercuric chloride.^{78, 79}



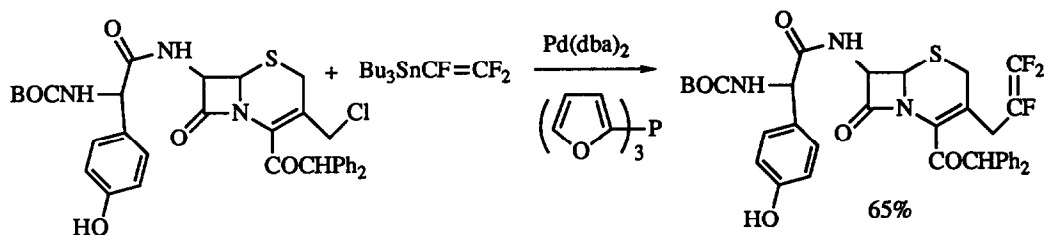
Trifluorovinyltin derivatives react with sulfur dioxide. However, low yields of the product from insertion into the tin-carbon bond of the trifluorovinyl group were found.⁸⁵



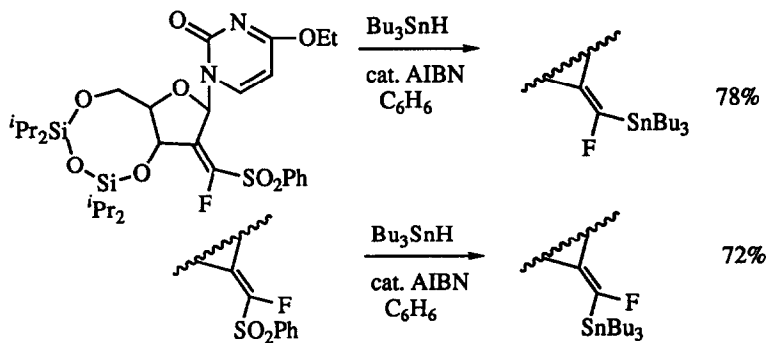
Trialkyl(trifluorovinyl)stannanes readily undergo Stille coupling reactions.⁸⁶ Reaction of tributyltrifluorovinyltin reagent with aryl iodides catalyzed by palladium gave trifluorovinylbenzene derivatives. The reaction could be carried out in a variety of solvents. The product yield increased in the order: HMPA~DMF>DMSO>THF>C₆H₆>C₂H₄Cl₂.



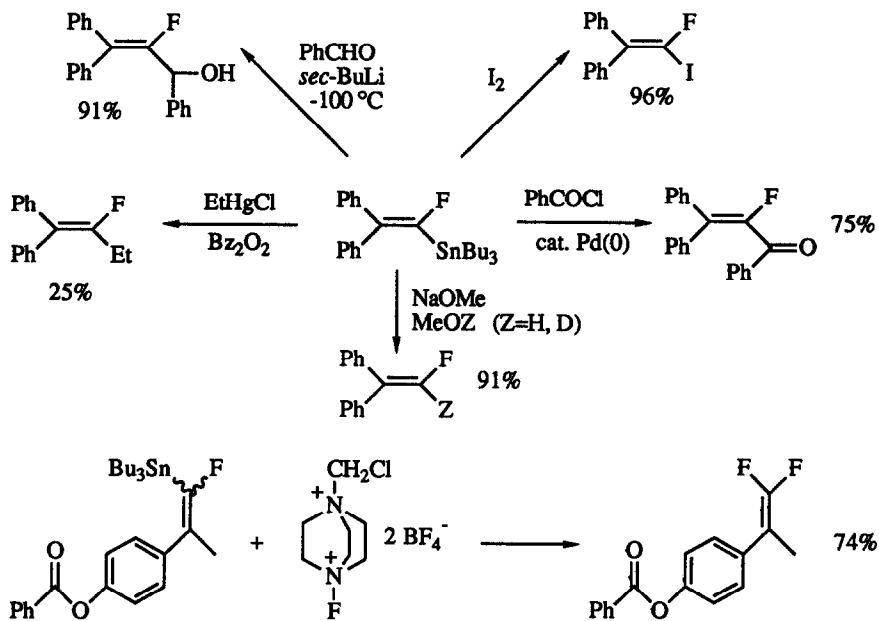
Recently, 3-trifluorovinylmethylcephem and 3-trifluorovinylcephem were prepared in good yields from the reaction of tributyl(trifluorovinyl)stannane with 3-vinyl triflate or 3-chloromethylcephem. The coupling reaction was catalyzed by a palladium catalyst containing the tri(2-furyl)phosphine ligand.^{87, 88}



Radical reaction of *E*- or *Z*- α -fluorovinylsulfones with two equivalents of tributyltin hydride gave α -(fluorovinyl)stannanes with retention of stereochemistry.



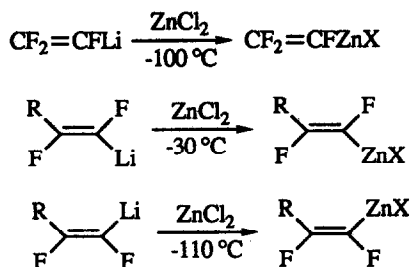
A wide variety of fluorovinylsulfones have been prepared by McCarthy and co-workers. Stereospecific destannylation reactions of the α -fluorovinyl stannanes include protonolysis,⁹⁰ deuterolysis,⁹⁰ acylation,⁹¹ iodination⁹¹ and electrophilic fluorination.⁹² Reaction with benzaldehyde and *sec*-butyllithium at low temperature afforded the allylic alcohol.⁹¹ Reaction with ethylmercuric chloride and benzoyl peroxide gave the ethyl derivative in low yield.⁹¹



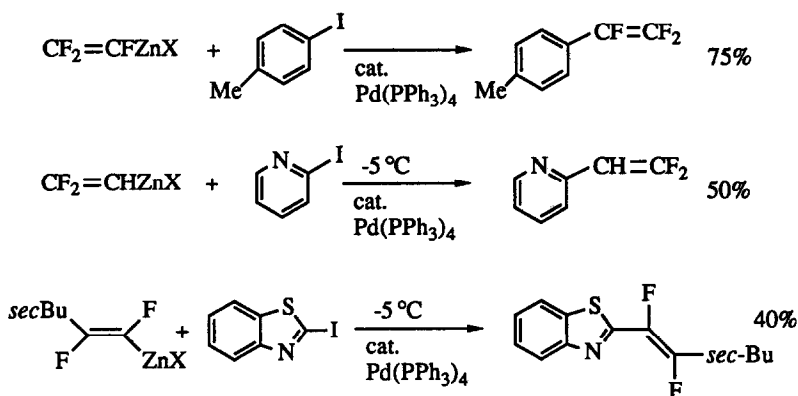
4. Fluorovinyl Zinc Reagents

Since the synthetic utility of fluorinated vinyl lithium and Grignard reagents has been impeded by the restricted thermal stability of these reagents, alternative organometallic reagents such as zinc reagents which might exhibit superior thermal behavior and chemical reactivity are desirable. Fluorinated vinylzinc reagents can be prepared by two methods: 1) capture of the corresponding vinyl lithium reagent at low temperatures with a zinc salt, or 2) direct insertion of zinc into the carbon-halogen bond of a vinyl halide.

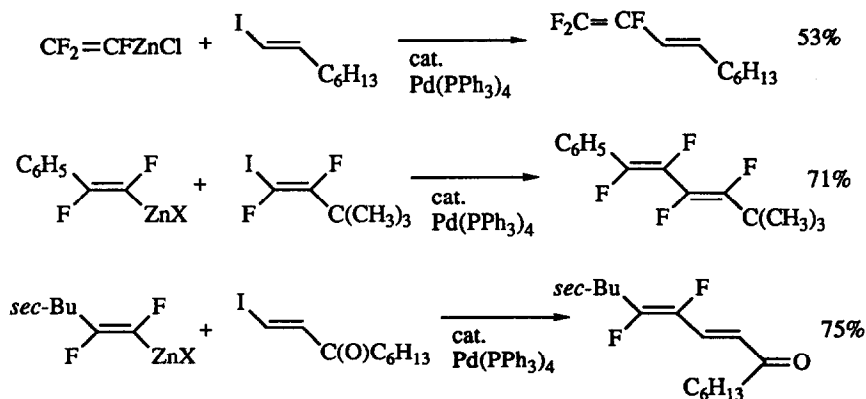
The first method involves the generation of the vinyl lithium at low temperature from the corresponding fluorinated vinyl halides or hydroalkenes.¹² Addition of zinc halides to the lithium reagent solution gives the stable vinylzinc halides in excellent yields.^{12,86,93,94,95,96,97,98,99,100,101,102} The reaction temperatures are a function of the thermal stability of the vinyl lithium reagent. Trifluorovinyl, 2,2-difluorovinyl and 1-chloro-2-fluorovinyl as well as *E*-1,2-difluoroalkenylzinc chlorides were generated at temperatures below $-100\text{ }^\circ\text{C}$, while some *Z*-1,2-difluoroalkenylzinc chlorides could be prepared in ether at $-30\text{ }^\circ\text{C}$.⁹⁵ Pentafluoropropen-2-ylzinc has been prepared by this method.²⁸



In the presence of palladium catalyst, these fluorinated vinylzinc reagents undergo coupling with phenyl or heterocyclic iodides to give the corresponding fluorinated vinyl derivatives. The coupling reaction proceeded smoothly in THF at or near room temperature. Typical examples are outlined below:

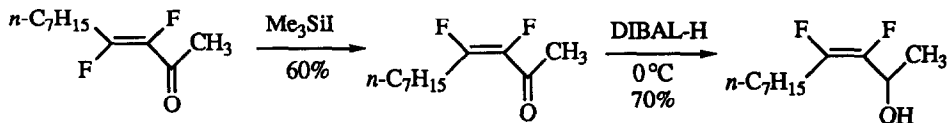


A variety of vinyl iodides, including non-fluorovinyl and fluorovinyl as well as functionalized vinyl iodides, react with fluorovinylzinc chlorides catalyzed by palladium to provide fluorinated dienes. In all cases, the stereoisomeric purity of the product is high. This procedure is particularly useful to prepare fluorinated polyenes.

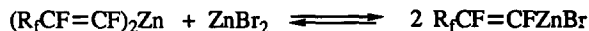


chloroformate. Yields were generally good and the stereochemistry of the vinylzinc reagent was preserved.

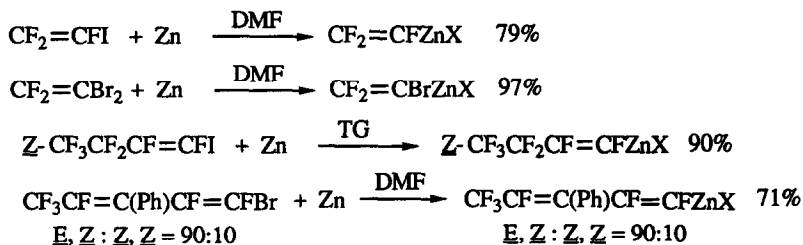
A *trans*- α,β -difluoro- α,β -unsaturated ketone readily undergoes isomerization upon treatment with trimethylsilyl iodide to form *cis*- α,β -difluoro- α,β -unsaturated ketones. Subsequent reduction with DIBAL-H gave *cis*- α,β -difluoroallyl alcohols.^{101, 102}



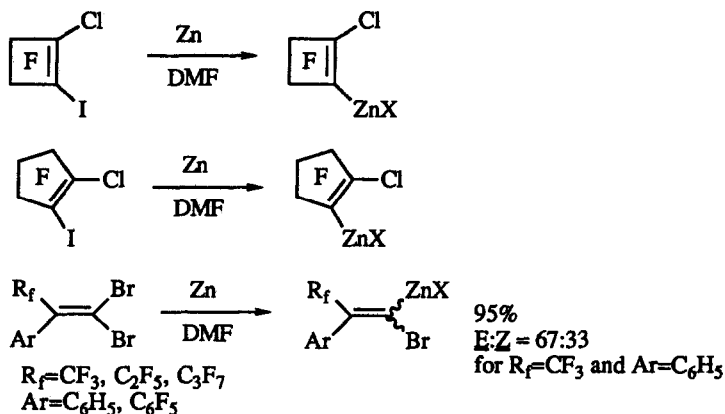
The second method for the preparation of fluorinated vinylzinc reagents involves the direct reaction of fluorovinyl bromides or iodides with acid-washed zinc.¹⁰⁴ Though the starting vinyl halide is more expensive, the procedure is general, straightforward and has the advantage of avoiding low temperatures. The fluorinated vinylzinc reagents can be prepared from vinyl iodides in a variety of solvents such as DMF, DMAC, triglyme, tetraglyme, THF and acetonitrile.¹⁰⁴ In general, vinyl bromides required more polar solvents than vinyl iodides.¹⁰⁴ Alternatively a less polar solvent can be used with a two-fold excess of a strongly coordinating ligand such as TMEDA.^{105, 106} Fluorinated vinyl iodides gave the zinc reagents in excellent yields at room temperature. Vinyl bromides reacted readily with acid-washed zinc in DMF at room temperature to 60 °C.¹⁰⁴ The induction periods for these reactions varied from a few seconds to several minutes. The zinc reagents were formed as a mono/bis mixture, whose ratio varied with the structure of the vinyl halide and solvent. The mono/bis zinc reagents were distinguished by ¹⁹F NMR analysis. Upon addition of the appropriate zinc halide, the signal for the mono reagent was observed to increase at the expense of the signal for the bis reagent, according to the following equilibrium:



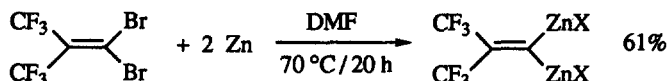
Typical examples for the preparation of perfluoroalkenylzinc reagents follow:¹⁰⁴



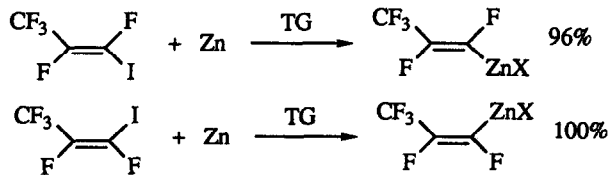
More recently, four-, five- and six-membered cyclic fluorinated vinylzinc reagents^{107, 108, 109} as well as a series of α -bromofluorovinylzinc reagents^{104, 110, 111} have been prepared using this methodology.



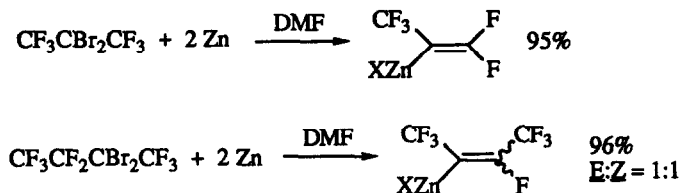
The carbon-bromine bond of the α -bromozinc reagents was unreactive towards a second zinc insertion reaction. Treatment with excess zinc under more forcing conditions resulted only in decomposition products. However, the bis-zinc reagent could be prepared from $(\text{CF}_3)_2\text{C}=\text{CBr}_2$.^{111, 112}



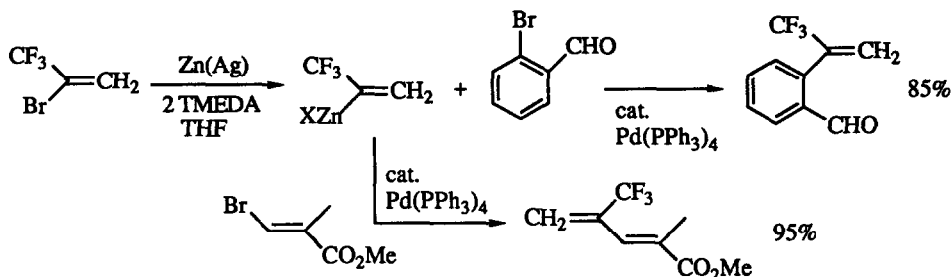
The stereochemical integrity of the perfluoroalkenyl halides is preserved in the preparation of zinc reagents. For example, *E*- or *Z*-perfluoropropenyl iodides react with zinc in TG to form the corresponding *E*- or *Z*- zinc reagents, respectively.^{104, 113}



The 2-pentafluoropropenylzinc reagent could be prepared in high yield *via* a novel one-pot reaction of 2,2-dibromohexafluoropropane and two equivalents of zinc in DMF.^{28, 114} When a 1:1 ratio of $\text{CF}_3\text{CBr}_2\text{CF}_3$: Zn was allowed to react, a mixture of the zinc reagent and unreacted $\text{CF}_3\text{CBr}_2\text{CF}_3$ was observed. A reasonable mechanism for the zinc reagent formation involves dehalogenation of $\text{CF}_3\text{CBr}_2\text{CF}_3$ to form $\text{CF}_3\text{CBr}=\text{CF}_2$ in a slow step, followed by fast insertion of zinc into the carbon-bromine bond of the vinyl bromide. However, reaction in acetonitrile, THF, ether, dioxane or triglyme, gave only complex mixtures. A similar reaction of $\text{CF}_3\text{CF}_2\text{CBr}_2\text{CF}_3$ with Zn in DMF gave a 1:1 ratio of the *E*- and *Z*- isomers of the *internal* vinylzinc reagent, $\text{CF}_3\text{CF}=\text{C}(\text{CF}_3)\text{ZnX}$. No terminal zinc reagent was observed.¹¹⁵

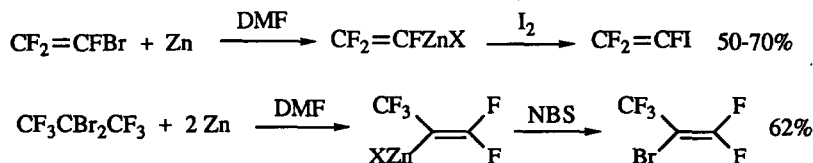


Another rare *internal* fluorinated zinc reagent was recently prepared by the reaction of $\text{CF}_3\text{CBr}=\text{CH}_2$ with $\text{Zn}(\text{Ag})$ in THF.¹⁰⁵ This partially fluorinated zinc reagent was successfully coupled with functionalized vinyl¹⁰⁶ and aryl halides in the presence of a palladium catalyst.¹⁰⁵



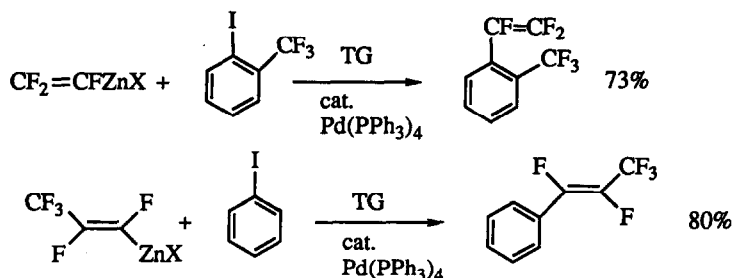
The fluorinated zinc reagents exhibit exceptional thermal stability.¹⁰⁴ A sample of $\text{Z-CF}_3\text{CF}=\text{CFZnX}$ in triglyme showed no loss of activity after three days at room temperature and only 10% of the zinc reagent decomposed after 36 days at room temperature. Only 5% of the zinc reagent decomposed when heated at 65 °C for three days. A 25% loss of activity was observed at the same temperature after 36 days. This excellent thermal stability permits these zinc reagents to be used on a large scale and over an extended period of time in a variety of synthetic reactions without any significant change in reactivity.

Terminal or internal perfluoroalkenylzinc reagents reacted with acids to give the corresponding hydroperfluoroalkenes.^{28, 104} Treatment with bromine or NBS afforded the alkenyl bromides.¹¹⁴ With iodine, the zinc reagents produced perfluoroalkenyl iodides in excellent yields. This provides a new and convenient preparation of perfluoroalkenyl iodides from the corresponding bromides.^{104, 114}

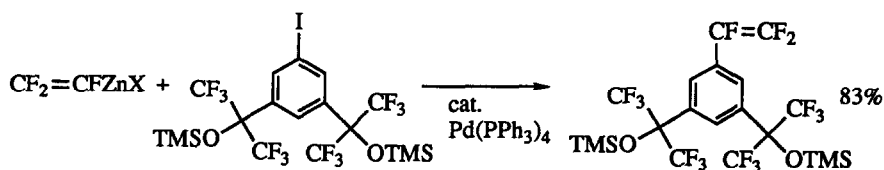


Fluorovinylzinc reagents react with aryl iodides in the presence of $\text{Pd}(\text{PPh}_3)_4$ to give the corresponding fluorinated vinyl arenes in good yields under mild conditions.^{105, 113, 114, 115} A wide variety of substituted aryl iodides readily participate in the coupling process. Aryl substituents that have been tolerated by this methodology include NO_2 , F, Cl, Br, I, OMe, CF_3 , $\text{C}(\text{R}_f)=\text{CF}_2$ ($\text{R}_f=\text{F}$, CF_3), $\text{C}(\text{O})\text{CH}_3$, OAc and CO_2Et . Good yields of coupled products were obtained with bulky substituents such as isopropyl, trifluoromethyl and

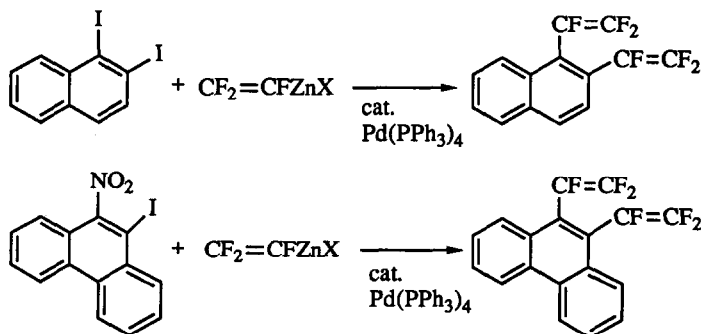
nitro, in the ortho position with terminal vinylzinc reagents and the partially fluorinated vinylzinc reagent, $\text{CF}_3\text{C}(\text{ZnX})=\text{CH}_2$. However, the bulky, internal vinylzinc reagent $\text{CF}_3\text{C}(\text{ZnX})=\text{CF}_2$ did not react to completion with any ortho substituents larger than a fluorine atom.¹¹⁴ In general, aryl bromides required higher reaction temperatures than their iodo- counterparts, and usually resulted in lower conversions and yields. An exception are the excellent results achieved by Xu with aryl bromides.¹⁰⁵ No reaction was observed in the presence of nickel catalysts such as $\text{Ni}(\text{PPh}_3)_4$ or $\text{Ni}[\text{P}(\text{OEt})_3]_4$.¹¹³



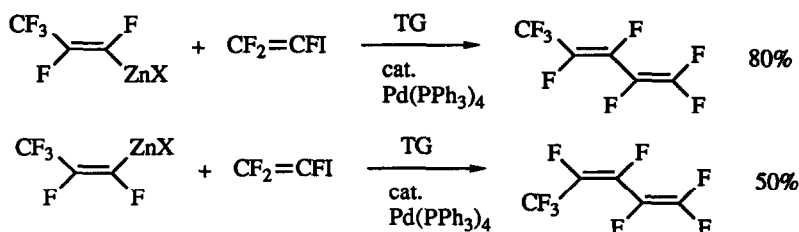
Sprague and co-workers have employed this methodology in the synthesis of a fluorinated styrene derivative.¹¹⁶



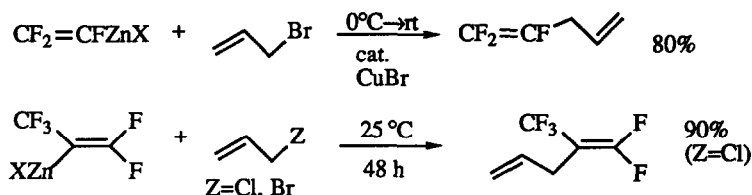
5-Iodouracil¹¹⁷ and salicylic acid¹¹⁸ derivatives have also been functionalized with trifluorovinylzinc. More recently, 1,2-diiodonaphthalene was coupled with 2 equivalents of trifluorovinylzinc reagent to give 1,2-bis(trifluorovinyl)naphthalene. Surprisingly, 9,10-bis(trifluorovinyl)phenanthrene was formed under similar conditions when 9-iodo-10-nitrophenanthrene was used as a substrate.¹¹⁹



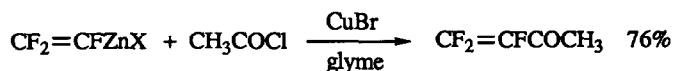
Perfluorodienes are readily prepared by the palladium-catalyzed reaction of the trifluorovinylzinc reagent with perfluorovinyl iodides.^{120, 121} These coupling reactions proceeded at 80 °C in TG. No reaction was observed at room temperature in contrast to the corresponding reaction of fluorinated vinylzinc chloride with vinyl iodides in THF.⁹⁶ The products were readily isolable from the solvent by distillation and stereoisomeric purity was excellent. These compounds were useful models for probing the thermal electrocyclic interconversions of perfluorodienes and perfluorocyclobutenes.¹²¹



Vinylzinc reagents undergo slow (2-3 days) allylation reaction with allyl halides at room temperature.^{287, 122} However, the coupling reaction could be catalyzed by cuprous halides to afford high yields of fluorinated dienes in an exothermic reaction.¹²² With substituted allyl halides, $\text{CF}_3\text{C}(\text{ZnX})=\text{CF}_2$ gave products of both α and γ -attack with preference for attack at the less hindered position.²⁸

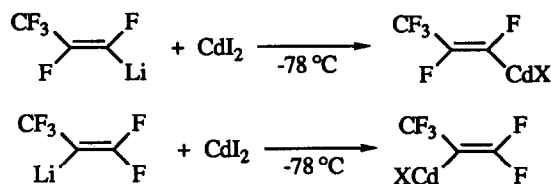


Acylation of trifluorovinylzinc reagents can also be accomplished with cuprous bromide catalysis.¹²³ A variety of aliphatic acid chlorides gave good yields of the corresponding ketones. Although the vinylzinc



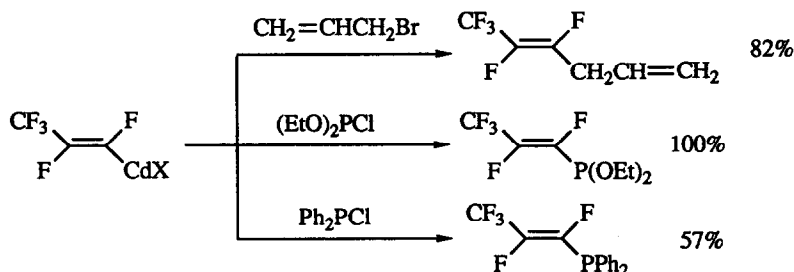
reagents can be prepared in a number of aprotic solvents such as DMF, glymes and THF, it is necessary to utilize the glyme system for this acylation reaction. The acylation reaction occurs in DMF; but, the electron deficient trifluorovinyl ketone products are immediately attacked by DMF and destroyed. Reaction of trifluorovinyl zinc reagents with perfluoro acid chlorides resulted in decomposition products. The internal trifluorovinylzinc reagent $\text{CF}_3\text{C}(\text{ZnX})=\text{CF}_2$ was again much less reactive than its terminal cousins. However, the α,β -unsaturated ketone products that formed were much more reactive due to the greater electron-withdrawing ability of the CF_3 vs. the fluorine atom. This zinc reagent only gave an isolable product upon reaction with pivaloyl chloride. Low conversions and/or inseparable side products were realized with propionyl, benzoyl, pentanoyl, and perfluorobutanoyl chlorides.¹²⁴

Alternatively, metathesis of the perfluoroalkenyllithium with cadmium halides gives the cadmium reagents. However, this method necessitates the regeneration of an unstable perfluoroalkenyllithium at low temperature.^{28, 126}



Perfluoroalkenylcadmium reagents, like their zinc counterparts, exhibit remarkable thermal stability. At room temperature, cadmium reagents are stable for months and at 100 °C, only very slow decomposition is observed.¹²⁵ Solvent (DMF or TG) complexes of bis(trifluorovinyl)cadmium and bis(perfluoropropenyl)cadmium can be isolated by distillation of the reaction mixture, followed by recrystallization from dichloromethane and pentane (1 : 5).¹²⁵ No reaction was observed between $\text{CF}_3\text{C}(\text{MX})=\text{CF}_2$ (M=Zn or Cd) and dry O_2 at room temperature.¹²⁷

Despite their impressive stability, perfluoroalkenylcadmium reagents are chemically reactive. Allylation of the reagents with allyl bromide gives the fluorinated 1,4-dienes. Reactions with $(\text{EtO})_2\text{PCl}$ and Ph_2PCl produce phosphorus derivatives.^{125, 126}

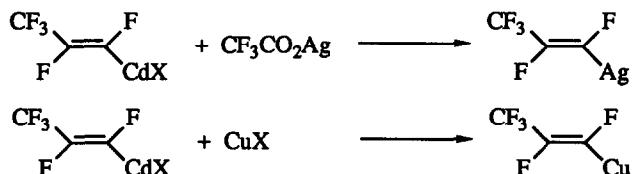


Non-fluorine containing organocadmium reagents have been utilized for the preparation of ketones from acid halides. However, pentafluoropropenylcadmium reagents did not react with acid chlorides in HMPA. When DMF was used as solvent, no ketone was obtained and a bis(pentafluoropropenyl)-substituted amine was instead formed in high yield.^{125, 126}



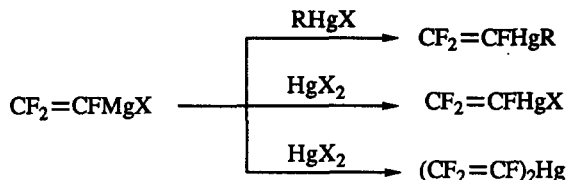
Perfluoroalkenylcadmium reagents readily undergo metathesis reactions with metal halides. *Z*-Pentafluoropropenylcadmium reagent was treated with silver trifluoroacetate in DMF to give the corresponding

vinylsilver in 91% yield.¹²⁶ With cuprous halides, a variety of vinylcopper reagents could be prepared in high yields.¹²⁸

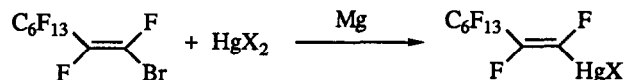


6. Fluorovinyl Mercury Reagents

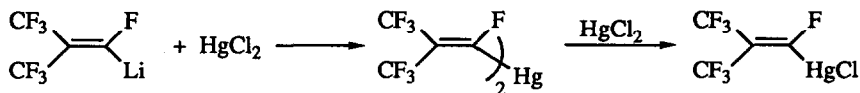
Trifluorovinylmercury derivatives are readily prepared from other trifluorovinylmetallic reagents,^{9,50,79} including Grignard reagents.⁷⁸ A variety of trifluorovinylmercury compounds can be obtained when trifluorovinylmagnesium halide reacts with either alkylmercury halides or mercury dihalides.



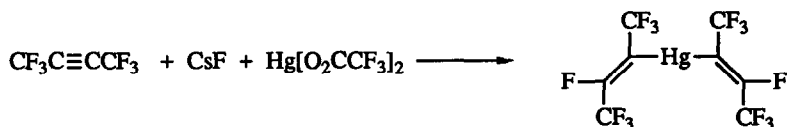
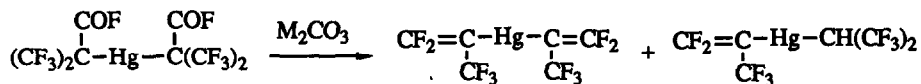
This methodology can also be applied to synthesize alkyl, aryl and haloperfluoroalkenylmercurials as well as bis(perfluoroalkenyl)mercurials. The yields of vinylmercurials could be improved using Barbier conditions.⁷⁸



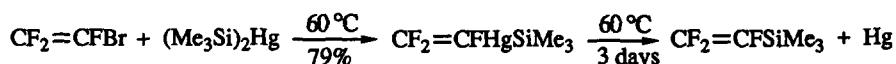
Trifluorovinyl lithium⁹ and trifluorovinyl tin^{78, 79} compounds were also utilized to prepare bis(trifluorovinyl)mercury. Perfluoro-2-methylpropenyl lithium and mercury dichloride gave the corresponding vinylmercury derivatives.¹⁹



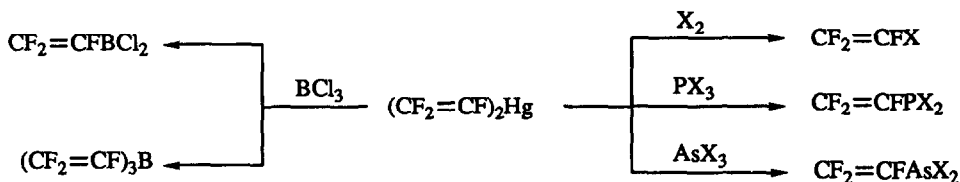
Deacylation of α, α' -mercuric bis(perfluoroisobutyryl) fluoride with sodium or potassium carbonate gives a 55:35 mixture of bis(perfluoro-2-propenyl)mercury and perfluoro-2-propenylperfluoro-2-H-2-propylmercury.¹²⁹ In the presence of a mercury salt, treatment of 2-hexafluorobutyne with cesium fluoride stereospecifically affords E-bis(hexafluoro-2-butenyl)mercury.¹³⁰



Photochemical or thermal reaction of trifluorovinyl bromide with bis(trimethylsilyl)mercury gave the vinyl mercury reagent. Prolonged heating or irradiation of the reaction mixture converted this reagent to trifluorovinylsilane and mercury metal.¹³¹



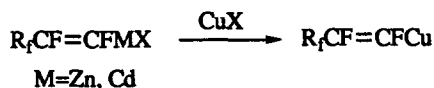
Perfluoroalkenylmercurials are thermally stable and can be purified by distillation. Bis-(trifluorovinyl)mercury reacts with halogens and group V trihalides to give trifluorovinylated compounds in good yields.⁵⁰ Similar reaction with varying proportions of BCl_3 gave tris(trifluorovinyl)boron and trifluorovinylboron dichloride.



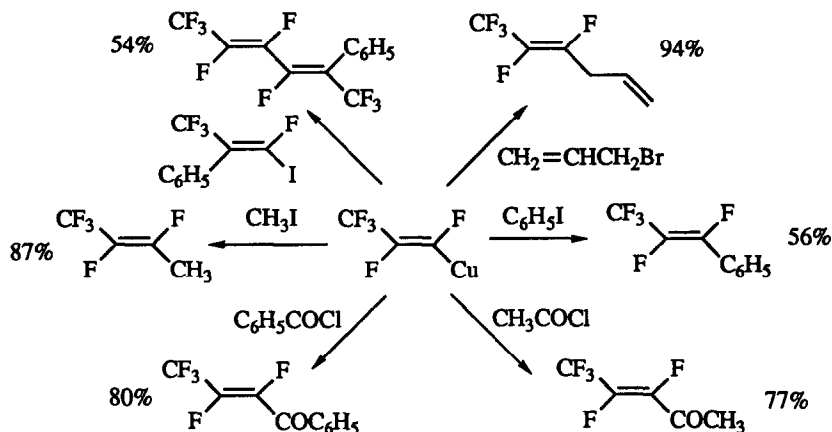
The tris(trifluorovinyl)aluminum-triethylamine complex can be obtained by the reaction of bis(trifluorovinyl)mercury with an aluminum hydride-triethylamine adduct in ether at -20°C . The trifluorovinylaluminum compound is a liquid which is easily oxidized in air.¹³²

7. Fluorovinyl Copper Reagents

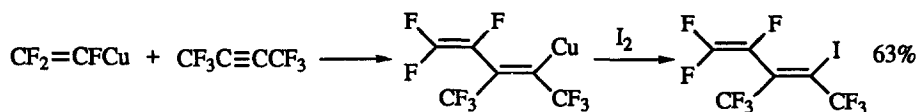
Attempted preparation of trifluorovinylcopper from reaction of trifluorovinyl iodide with copper metal was unsuccessful. Only a dimerization reaction took place and this reaction has been used for the synthesis of symmetrical perfluorodienes and polyenes. Trifluorovinylcopper is proposed as an intermediate, although it is not observed. It appears that the slow step in the coupling reaction is the reaction of trifluorovinyl iodides with copper to form the presumed trifluorovinylcopper, which then couples in a fast step with vinyl iodide to give the dimeric product.¹³³ In the case of the dimerization of $(\text{CF}_3)_2\text{C}=\text{CICF}_3$, the formation of a cyclobutene rather than a diene cannot be unequivocally excluded.¹³⁴



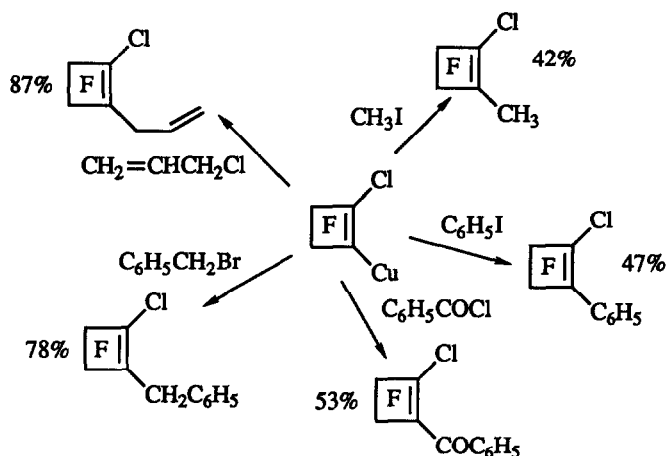
The trifluorovinylcopper reagents exhibit excellent stability at room temperature in the absence of oxygen and moisture. The decomposition rate increases at 50 °C. Trifluorovinylcopper reagent participates in coupling reactions with methyl, allyl, vinyl, alkanoyl and aryl halides.¹²⁸



Trifluorovinylcopper readily adds to perfluoroalkynes. Quenching of the adduct with acid or iodine affords the stereospecific *syn* addition product; no *anti* adduct is detected.^{126, 133}



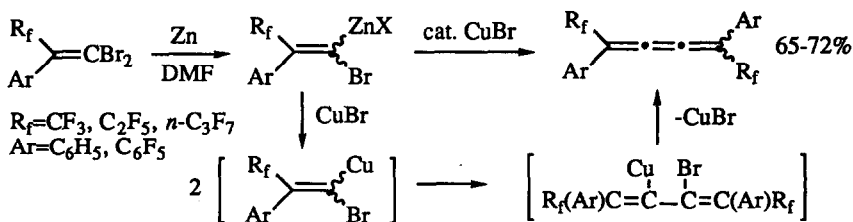
More recently, preparation of cyclic perfluoroalkenylcopper reagents have been reported by Choi and co-workers.^{107, 108, 109} Perfluorocycloalkenyl iodides reacted with zinc in DMF to give vinylzinc derivatives. Subsequent metathesis with cuprous halides gave the corresponding vinylcopper reagents, which also exhibited high thermal stability and readily underwent functionalization reactions. Perfluoro-2-chlorocyclobutenyl, pentenyl and hexenyl coppers reacted with allyl, benzyl, methyl and phenyl halides to produce the corresponding coupled products in moderate yields. With acid chlorides, the cycloalkenylcopper afforded the fluorinated ketones. A variety of acid chlorides including aliphatic, aryl and heterocyclic acid chlorides gave moderate yields of the corresponding α,β -unsaturated ketones. The acylation reaction could also be accomplished with the perfluorocycloalkenylzinc reagents with cuprous bromide catalysis.



Fluorocycloalkenylcopper reagents also couple smoothly with fluorocycloalkenyl iodides.¹⁴³

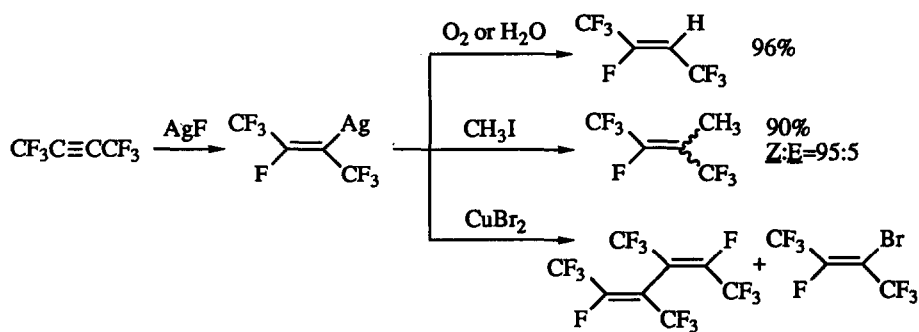


In contrast to the stability of the vinylcopper reagents with an α -fluorine, metathesis of fluorinated α -bromovinylzinc reagents with cuprous bromide in DMF does not generate an observable α -bromovinylcopper reagent. Instead, dimerization occurs and cumulene isomers are obtained.¹¹⁰ A nucleophilic attack / β -elimination mechanism has been proposed, based on low temperature ^{19}F NMR observations and a trapping experiment.¹¹¹ The *E*- and *Z*-cumulenes could be separated by silica gel chromatography or fractional recrystallization ($R_f = \text{CF}_3$, $\text{Ar} = \text{C}_6\text{F}_5$) and the structures were assigned by X-ray analysis. The α -Cl copper reagent, $\text{CF}_3(\text{Ph})\text{C}=\text{CClCu}$, was found to decompose by a similar pathway to afford butatrienes, albeit at a slower rate. The analogous α -F copper reagent decomposed by an oxidative dimerization pathway to give $[\text{CF}_3(\text{Ph})\text{C}=\text{CF}]_2$ isomers and no butatriene was detected.

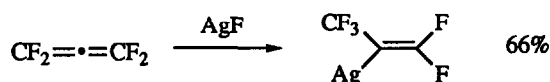


8. Fluorovinyl Silver Reagents

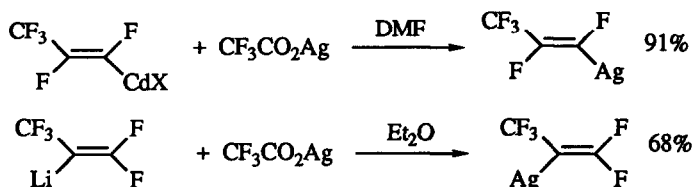
The first fluorovinylsilver compound was prepared by Miller and co-workers from the reaction of hexafluorobutyne with silver fluoride in acetonitrile. Unlike $\text{CH}_2=\text{CHAg}$, which decomposed at room temperature, *trans*- $\text{CF}_3\text{CF}=\text{C}(\text{Ag})\text{CF}_3$ was thermally stable and was isolated by sublimation in *vacuo* at temperatures up to 175 °C.¹⁴⁴ The crystal structure of $[\text{CF}_3\text{CF}=\text{C}(\text{CF}_3)\text{Ag}]_4$ was recently determined.¹⁴⁴ The silver reagent was also studied as a chemical vapor deposition precursor for silver films. Chemical transformations and spectroscopic analysis have confirmed that only the *trans*-vinylsilver isomer was formed. The vinylsilver was readily attacked by water and oxygen in solution and reacted with methyl iodide. Oxidation with cupric bromide afforded the symmetrical diene and *trans*-2-bromoheptafluoro-2-butene.¹⁴⁴



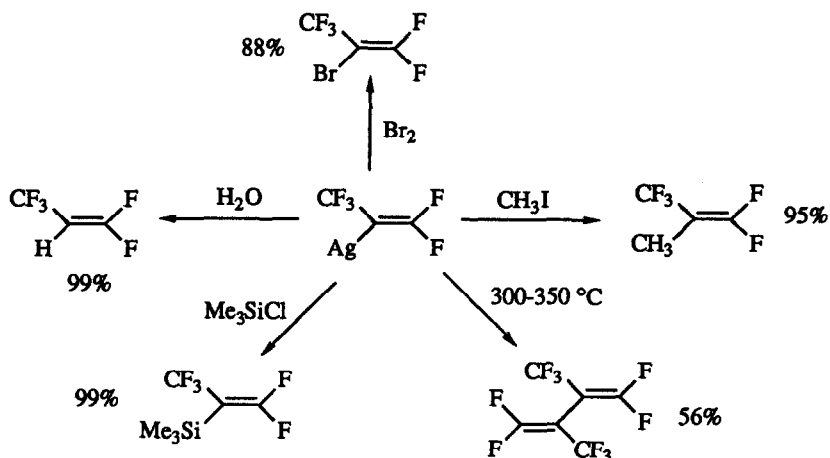
A similar addition reaction of silver fluoride to tetrafluoroallene in acetonitrile gave pentafluoropropen-2-ylsilver, which could be isolated in 66% yield by vacuum sublimation.¹⁴⁵



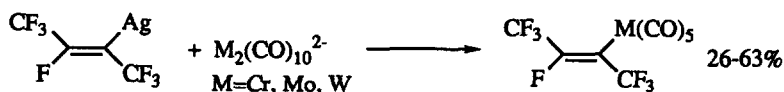
Metathesis of pentafluoropropenylcadmium reagent or pentafluoropropen-2-yllithium with silver trifluoroacetate also produced the corresponding vinyl silver reagents in excellent yields.²⁸



The silver reagents react with electrophiles such as water, halogens, organic halides and trimethylsilyl chloride to afford the trifluorovinylated products in excellent yields.¹⁴⁵ Pyrolysis of trifluorovinylsilver resulted in dimerization to the diene.¹⁴⁵



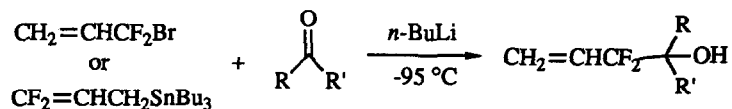
trans-Perfluoro-1-methylpropenylsilver reacts with the dinuclear metal carbonyl anions, $M_2(CO)_{10}^{2-}$ ($M=Cr, Mo, W$).¹⁴⁶



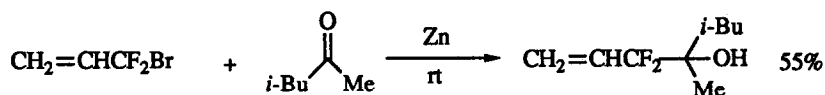
9. Fluorinated Allylmetallics

A. Difluoroallyl- and Difluoropropargylmetallic Reagents

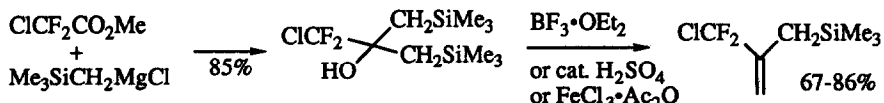
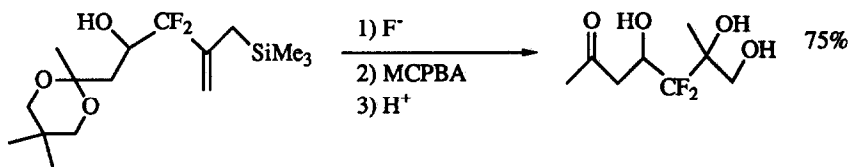
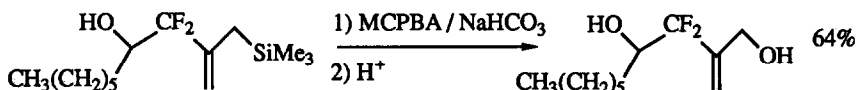
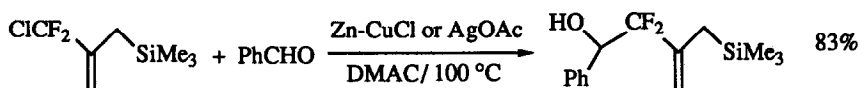
Although pregenerated α,α -difluoroallyllithium has not been observed, Seyferth reacted difluoroallyltin reagents with *n*-butyllithium in the presence of carbonyl substrates at $-95\text{ }^\circ\text{C}$ to give α,α -difluorohomoallylic alcohols.¹⁴⁷ The difluoroallyllithium was proposed as an intermediate. Later, 3-bromo-3,3-difluoropropene, a commercially available material, was also utilized to generate transient α,α -difluoroallyllithium.^{148, 149} Upon treatment of 3-bromo-3,3-difluoropropene with *n*-butyllithium and triorganosilyl chlorides in a mixture of ether, THF and pentane at $-95\text{ }^\circ\text{C}$, the corresponding α,α -difluoroallylsilanes were obtained. Carbonyl compounds could also trap the unstable difluoroallyllithium to provide the α,α -difluorohomoallylic alcohols.^{150, 151, 152} This procedure gives reasonable yields with dialkyl ketones, aryl alkyl ketones and aliphatic aldehydes, but low yields of α,α -difluorohomoallylic alcohols are obtained with aromatic aldehydes, α,β -unsaturated aldehydes and diaryl ketones, due to competitive reaction of *n*-butyllithium with the carbonyl compounds.



An attempt to prepare difluoroallylzinc from the reaction of 3-bromo-3,3-difluoropropene and zinc either in THF or in DMF was also unsuccessful. However, in the presence of zinc, 3-bromo-3,3-difluoropropene or 3-iodo-1,1-difluoropropene reacted with carbonyl compounds to give the corresponding α,α -difluorohomoallylic alcohols in good yields at 0 °C to room temperature.¹⁵³ This reaction was successful with aliphatic and aromatic aldehydes, dialkyl ketones and alkyl aryl ketones. Reaction with α,β -unsaturated aldehydes and ketones yielded 1,2-adducts exclusively. Cadmium and tin could also be used to mediate gem-difluoroallylation.¹⁵⁴



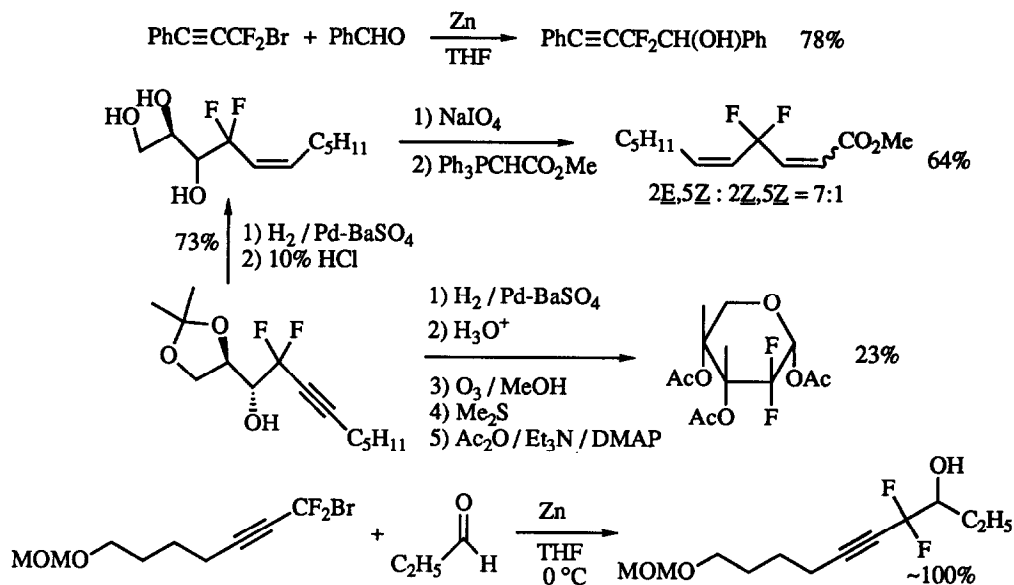
In a recent report, Ishihara demonstrated that gem-difluoroallylation of carbonyl compounds with 2-(trimethylsilyl)methyl-3-chloro-3,3-difluoropropene could be accomplished in the presence of Zn-CuCl or Zn-AgOAc in DMAC or DMF. THF and benzene were ineffective solvents.¹⁵⁵ Various aldehydes gave good yields of the gem-difluorohomoallyl alcohols, whereas the reaction with ketones was sluggish and afforded the desired products in only moderate yields. These products could be oxidized to give difluoro diols or triols. The starting material, 2-(trimethylsilyl)methyl-3-chloro-3,3-difluoropropene, was prepared from chlorodifluoroacetate by treatment with excess trimethylsilylmethylmagnesium chloride, followed by boron trifluoride etherate or sulfuric acid.



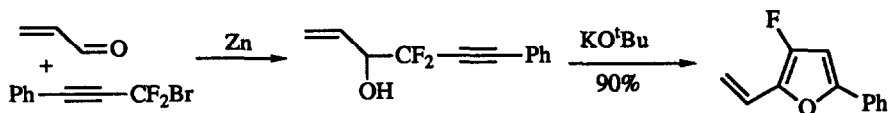
All products formed from the reaction of gem-difluoroallylmetallic reagents with carbonyl substrates result from exclusive attack of the CF₂ terminus at the carbon of the carbonyl group. In order to explain the

regioselectivity in the reaction of gem-difluoroallyllithium with carbonyl compounds, Seyferth proposed that the lithium ion would coordinate to the CH₂ terminus where the negative charge would be greatest, and would thus block the CH₂ terminus from attack by an electrophile relative to the "free" CF₂ terminus.¹⁴⁹ Seyferth's hypothesis may be questioned after close examination of gem-difluoroallylation with 3-bromo-3,3-difluoropropene and zinc or difluoroallylsilane and fluorides. Regardless of soft or hard carbonyl substrates, only the CF₂ terminus attacked the carbonyl carbon in the zinc-mediated reaction.¹⁵⁴ Though a catalytic amount of TASF-promoted reaction first formed "free" gem-fluoroallyl anion without a lithium ion block, α,α -difluorohomoallyl alcohols were still obtained exclusively.¹⁵⁰ These experimental results are in agreement with Tonachini's theoretical description, in which the electron distribution and HOMO polarization induced the reaction of both gem-difluoroallyllithium and "free" gem-difluoroallyl anion with both hard and soft carbonyls to give α -selective products.¹⁵⁶ Thus, the regiochemistry of gem-difluoroallylation can be rationalized in terms of attack of the more nucleophilic α -carbon of the gem-difluoroallyl intermediate.

Kobayashi reported the gem-difluoropropargylation of carbonyl substrates with zinc and 1-bromo-1,1-difluoro-2-alkynes, which were available by the reaction of lithium acetylides with CF₂BrCl¹⁵⁷ or CF₂Br₂.¹⁵⁸ When 1-bromo-1,1-difluoro-2-alkyne was slowly added to a mixture of zinc and aldehyde at 0 °C under argon, the α,α -difluoropropargyl alcohol was obtained in moderate to good yields, depending upon the aldehyde substrates.¹⁵⁸ The reaction at 40 °C gave a complex mixture. In the absence of aldehyde, no propargylzinc reagent was observed and only a symmetrical diacetylenic dimer was observed, even at low temperature. The 2,2-difluoropropargyl alcohols provided precursors for the preparation of fluorinated biologically active compounds, as outlined below.^{158, 159}



Similar methodology has also been recently employed to prepare 3-fluoro-2,5-disubstituted furans.¹⁶⁰



B. Perfluoroallylmetallic and Perfluorobenzylmetallic Reagents

Preparation of perfluoroallylmetallic reagents has recently been accomplished by Burton and co-workers. Initial attempts to prepare the perfluoroallylzinc reagent by reaction of perfluoroallyl iodide with zinc met with little success. Only a 7-14% yield of zinc reagent was detected by ^{19}F NMR. The major product isolated was perfluoro-1,5-hexadiene.¹⁶¹



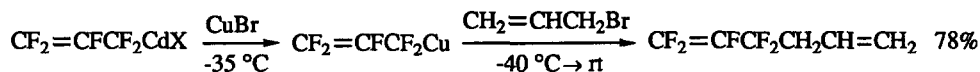
However, when perfluoroallyl iodide was reacted with cadmium in DMF at 0 °C, perfluoroallylcadmium reagent was formed in 71% yield.¹⁶¹



The cadmium reagent is thermally stable at -20 °C without any significant change in concentration after 40 days, but 58% of the reagent decomposes at room temperature after 7 days. In DMF the cadmium reagent decomposes rapidly to produce 3-hydroperfluoropropene when heated at 50 °C. Allylation of the cadmium reagent with allyl bromide at room temperature gave the fluorinated 1,5-hexadiene.



Direct preparation of perfluoroallylcopper from perfluoroallyl iodide with copper metal also met with little success. Again the only product obtained was perfluoro-1,5-hexadiene. However, metathesis of the cadmium reagent with cuprous bromide at -35 °C produced perfluoroallylcopper in 61% yield as determined by low temperature ^{19}F NMR analysis. The copper reagent is less thermally stable than its cadmium counterpart and decomposition products are detected at -30 °C. It also reacts with allyl bromide at -40 °C to give the fluorinated diene in good yield.¹⁶¹



The reagent $\text{C}_6\text{F}_5\text{CF}_2\text{CdX}$ could be prepared from direct reaction of $\text{C}_6\text{F}_5\text{CF}_2\text{Br}$ and acid-washed cadmium powder in DMF at room temperature.¹⁶² The cadmium reagent was stable at room temperature for several days but started to decompose at 50 °C. Like perfluoroallylcadmium, perfluorobenzylcadmium

underwent functionalization reactions. With iodine at room temperature, $C_6F_5CF_2CdX$ gave $C_6F_5CF_2I$ in good yield. The cadmium reagent also reacted with allyl bromide to afford $C_6F_5CF_2CH_2CH=CH_2$.

Attempts to prepare perfluorobenzylcopper by metathesis of $C_6F_5CF_2CdX$ with $CuBr$ at room temperature failed, presumably due to the low thermal stability of the copper reagent at room temperature. However, when $C_6F_5CF_2CdX$ was treated with $CuBr$ in DMF at $-35\text{ }^\circ\text{C}$, a rapid exchange reaction occurred and $C_6F_5CF_2Cu$ was formed in quantitative yield.¹⁶² The copper reagent was chemically active and reacted with allyl bromide at $-35\text{ }^\circ\text{C}$ to form $C_6F_5CF_2CH_2CH=CH_2$. The difluoromethylene moiety from CF_3Cu could also insert into the carbon-copper bond of $C_6F_5CF_2Cu$ to form $C_6F_5CF_2CF_2Cu$,¹⁶³ which had been previously prepared by reaction of C_6F_5Cu and CF_3Cu .¹⁶³ This finding implied that $C_6F_5CF_2Cu$ was an intermediate in the latter reaction.

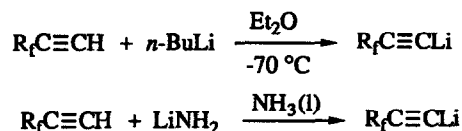
10. Perfluoroalkynylmetallics

Perfluoroalkynyl derivatives of metals and main group elements have largely been unexplored compared with their perfluoroalkyl and alkenyl analogs. In this part we briefly discuss preparation and application of typical perfluoroalkynylmetallic reagents.³

A. Perfluoroalkynyl Lithium, Magnesium and Tin Reagents

Terminal perfluoroalkyl acetylenes exhibit significant acidity due to the strong electron withdrawing ability of the perfluoroalkyl group. Upon treatment with strongly basic organometallic reagents, hydrogen-metal exchange occurs to give perfluoroalkynylmetallic compounds. This exchange reaction is particularly useful for the preparation of perfluoroalkynyllithium and Grignard reagents.

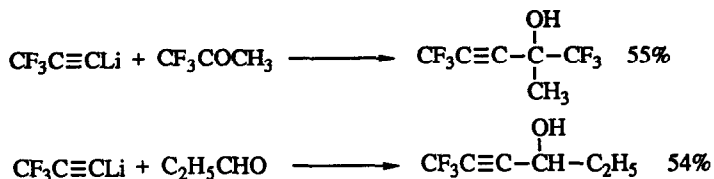
Perfluoroalkynyllithium could be readily prepared from the reaction of terminal perfluoroalkynes with *n*-butyllithium in ethereal solvents,¹⁶⁴ or lithium amide in liquid ammonia.¹⁶⁵ The lithium reagents were usually generated at temperatures below $-70\text{ }^\circ\text{C}$. They did not undergo extensive decomposition until exposed to temperatures greater than $0\text{ }^\circ\text{C}$.



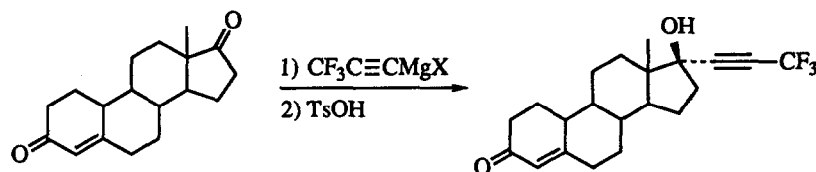
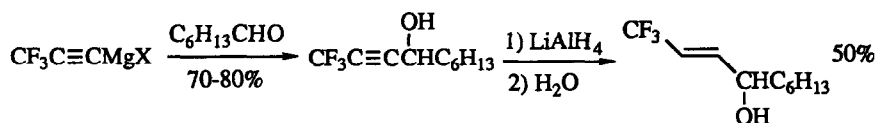
Trifluoropropynylmagnesium bromide was readily prepared from trifluoropropyne and ethylmagnesium bromide at room temperature in ether or THF.¹⁶⁶ Other organomagnesium reagents which have been employed for the preparation of fluoroalkynyl Grignard reagents include benzylmagnesium bromide, phenylmagnesium bromide, phenylmagnesium iodide and methylmagnesium iodide.^{167, 168, 169} The alkynylmagnesium reagents are more stable than the lithium analogs and no decomposition was observed in refluxing ether. The perfluoroalkynyllithium and magnesium reagents are also more stable than perfluoroalkyl and vinyl lithium or magnesium reagents. This is expected since there are no β -fluorines present which may undergo β -elimination.



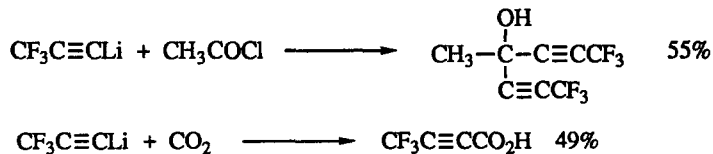
Perfluoroalkynyllithium and magnesium reagents readily attack the carbonyl groups of aldehydes and ketones.¹⁶⁴ Tarrant reacted the trifluoropropynyllithium with ketones to give the corresponding propargyl alcohols in moderate yields.



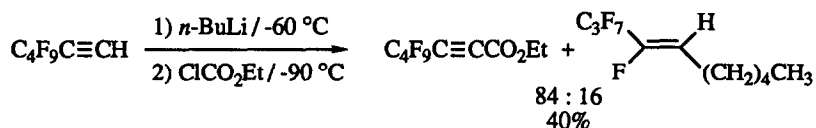
Kobayashi prepared trifluoromethyl propargyl alcohols from trifluoropropynylmagnesium bromide. The alcohols could be further elaborated by hydrometallation and Claisen rearrangement to provide key trifluoromethylated polyene intermediates with potential biological activity.¹⁷⁰ These reagents have also proven effective for introduction of the trifluoropropynyl functionality into the 17- α -position of steroidal hormones providing new analogs for biological testing.^{165, 171}



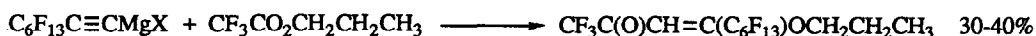
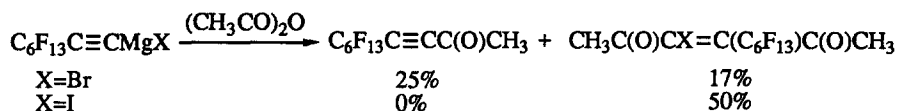
Acid chlorides or esters reacted with two equivalents of trifluoropropynyllithium to give bis(trifluoropropynyl)-substituted alcohols.¹⁶⁴ Treatment with chloroformates gave the trifluorobut-2-ynoate in low yield (39-43%), plus di(trifluoropropynyl) ketone and tris(trifluoropropynyl) alcohol.¹⁷² Carboxylation of the lithium reagent with carbon dioxide afforded the corresponding acid in 49% yield.¹⁷²



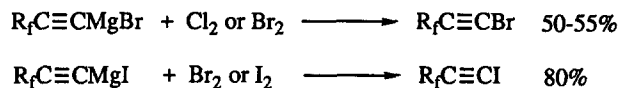
Longer chain perfluoroalkynyllithiums, prepared from *n*-butyllithium and perfluoroalkyne in THF at $-70\text{ }^{\circ}\text{C}$, were reported to react with chloroformates at $-90\text{ }^{\circ}\text{C}$ to give moderate yields of the acetylenic esters. A side product (11-16%) formed in these reactions was identified as $\text{R}'\text{CF}=\text{CH}(\text{CH}_2)_4\text{CH}_3$, where R' is one difluoromethylene unit shorter than the starting R_f group. The mechanism for the formation of this product is not clear, but it is evident that *n*-butyllithium adds to the starting alkyne.¹⁶⁴



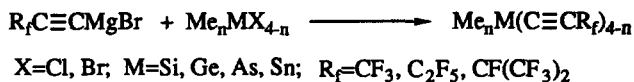
Attempts to acylate perfluoroalkynylmagnesium halides with acetic anhydride to prepare ynones met with little success. Although a small amount of ynone was observed upon reaction with perfluorooctynylmagnesium bromide, no desired ynone was obtained when perfluorooctynylmagnesium iodide was employed.¹⁷³ Reaction with *n*-propyl trifluoroacetate resulted in the formation of an α,β -unsaturated ketone, which was probably formed by attack of propoxide on the expected ynone.¹⁷³



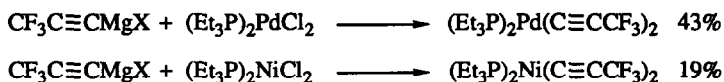
Reaction of perfluoroalkynylmagnesium bromide with either chlorine or bromine gives perfluoroalkynyl bromide in 50-55% yields. Treatment of perfluoroalkynyl magnesium iodide with bromine or iodine produces perfluoroalkynyl iodide in 80% yields. Thus, if the halogenating agent is a stronger oxidizing agent than the anion in its elemental state, the anion is oxidized to its elemental form which then halogenates the Grignard reagent.^{173, 174}



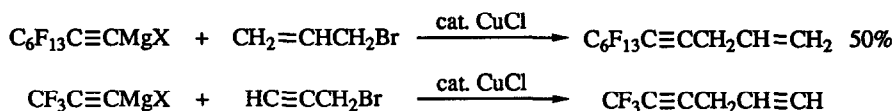
Perfluoroalkynyllithium and magnesium reagents have also been utilized to prepare a variety of perfluoroalkynyl substituted elemental and metallic compounds.^{168, 169} Reaction with organosilicon, germanium, arsine and tin halides gave the corresponding perfluoroalkynyl substituted derivatives. The tin derivatives are less stable hydrolytically and thermally than their non-fluorinated tin analogs. The difference between fluorinated alkynyltin and non-fluorinated alkynyltin reagents can be explained on the basis of the effect of the strong electron withdrawing effect of the fluoroalkyl group, which polarizes the tin-carbon bond, so that the tin atom is sufficiently electrophilic to undergo attack by water.



Trifluoropropynyllithium or magnesium halides have been used for the preparation of trifluoropropynylated transition metal complexes.¹⁶⁷

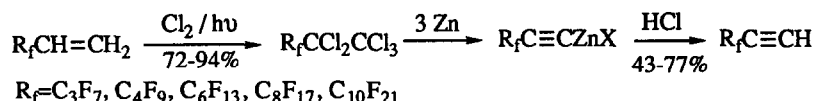


Coupling reactions of perfluoroalkynylmagnesium reagents with allyl halides are catalyzed by copper(I) halides to give perfluorinated enynes.¹⁷⁵

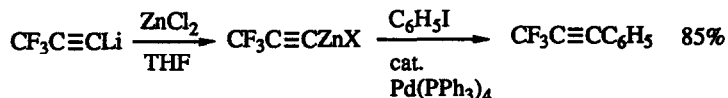


B. Perfluoroalkynyl Zinc and Cadmium Reagents

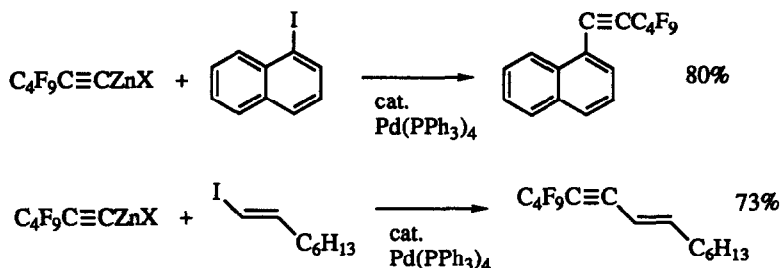
Finnegan and Norris first prepared trifluoropropynylzinc, CF₃C=CZnX, by direct reaction of 1,1,2-trichloro-3,3,3-trifluoropropene and excess zinc.¹⁷⁶ The zinc reagent was formed as a mixture of mono and bis(trifluoropropynyl)zinc. Addition of water to the zinc reagent solution gave trifluoropropyne in 75% yield. The zinc reagent could be oxidatively coupled with CuCl₂ to form perfluoro-2,4-hexadiyne, along with fluorochloroalkenes as byproducts.¹⁷⁷ Recently, the higher acetylenic homologues have been prepared by Burton and Spawn from 1,1,1,2,2-pentachloroperfluoroalkanes and zinc in DMF. The requisite pentachloro precursors were obtained from the corresponding commercially available 1,1,2-trihydroperfluoro-1-alkenes. Acid hydrolysis of these zinc reagents gave the perfluoroalkynes in good yields.¹⁷⁸



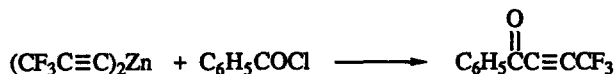
Metallation of perfluoroalkynyllithiums with zinc chloride in THF provides an alternative route to perfluoroalkynylzinc reagents.¹⁷⁹ The zinc reagents prepared by this approach exhibited greater reactivity towards palladium-catalyzed coupling reactions. Bumgardner first reported that trifluoropropynylzinc chloride reacted with aryl iodides in the presence of Pd(PPh₃)₄ to give aryl trifluoromethyl acetylene in high yields (>80%).¹⁷⁹ However, the zinc reagent directly prepared from 1,1,2-trichloro-3,3,3-trifluoropropene gave the coupled products in less than 40% yields.¹⁷⁹



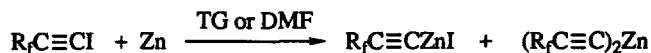
Recently, Yoneda reported that the longer perfluoroalkyl chain alkynylzinc reagents also underwent coupling reactions with aryl iodides.¹⁸⁰ However, the reaction with heteroaromatic iodides was sluggish and attempted coupling with bromobenzene only gave traces of product. Vinyl iodides and bromides also coupled with the zinc reagents in the presence of palladium catalyst to produce the corresponding enynes with retention of configuration.



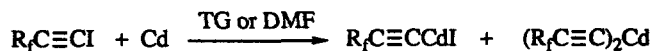
Bis(trifluoropropynyl)zinc reacted with benzoyl chloride without catalysis to give benzoyl-(trifluoromethyl)acetylene.¹⁸¹



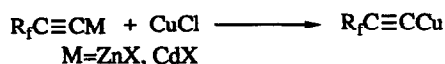
Burton and co-workers developed the direct metallation of 1-iodoperfluoro-1-alkynes for the preparation of perfluoroalkynylzinc reagents.¹⁸² When 1-iodoperfluoro-1-alkynes were treated with zinc in triglyme or DMF at room temperature the corresponding zinc reagents were formed in excellent yields as a mixture of mono and bis perfluoroalkynylzinc species. These could be readily distinguished by ¹⁹F NMR based on the enhancement of the signal for the mono species upon addition of zinc iodide.



Similarly, perfluoroalkynylcadmium reagents could also be prepared from cadmium and iodoperfluoroalkynes in DMF or TG.¹⁸² These reactions were conducted at room temperature and induction periods were less than 5 minutes. A mixture of mono and bis cadmium reagents were obtained in high yields.

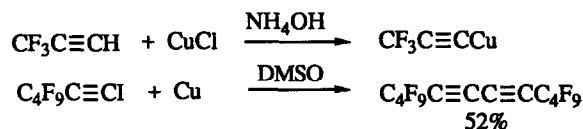


Perfluoroalkynylzinc and cadmium reagents exhibited good thermal stability.¹⁸² For example, $C_4F_9C\equiv CZnX$ in DMF solution showed only a 4% loss of activity after 36 days at room temperature. However, decomposition occurred upon heating to 100 °C. The perfluoroalkynylzinc reagents reacted with water or halogens to give perfluoroalkynes and perfluoroalkynyl halides, respectively. Although they did not react with acid chlorides or allyl halides, perfluoroalkynylzinc reagents readily underwent metathesis reactions with copper(I) halides in DMF to give the copper acetylides quantitatively.¹⁸²



C. Perfluoroalkynyl Copper, Mercury and Silver Reagents

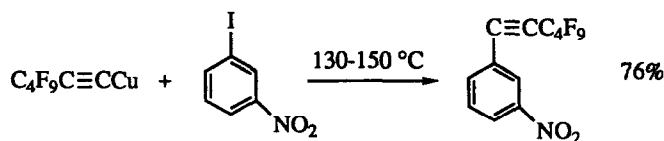
As indicated earlier, copper(I) chloride catalyzes the coupling reaction of perfluoroalkynylmagnesium bromides with allyl or propargyl bromides to give the coupled products.¹⁷⁵ Although the intermediate was not identified in this reaction it is obvious that perfluoroalkynylcopper must be involved. The first perfluoroalkynylcopper was prepared by Haszeldine, who treated trifluoropropyne with cuprous chloride / ammonium hydroxide to produce trifluoropropynylcopper, which was isolated and characterized by elemental analysis.¹⁸³ Direct preparation of perfluoroalkynylcopper from the corresponding iodide with copper metal in DMSO at room temperature was unsuccessful. The dialkyne was the major product.¹⁸²



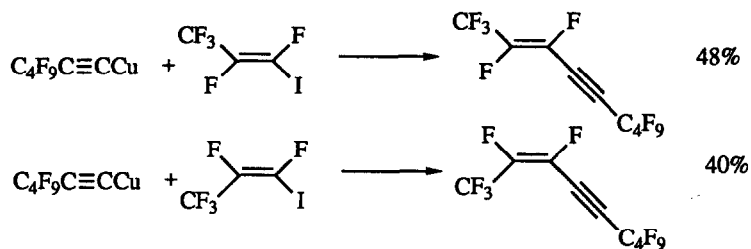
Metathesis of perfluoroalkynyl zinc reagents with cuprous halides provides a more convenient route to perfluoroalkynylcopper reagents. As discussed previously, the zinc reagents are formed from zinc and the corresponding pentachloroperfluoroalkane or 1-iodoperfluoroalkyne.¹⁸²



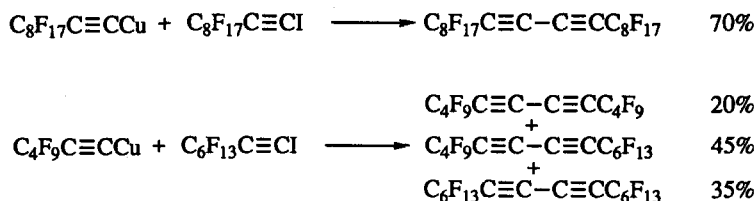
The perfluoroalkynylcopper reagents exhibit excellent thermal stability from room temperature to 65 °C. Trifluoropropynylcopper completely decomposes at 100 °C, while 85% of the more stable perfluorohexynylcopper remained after 19 hours at 100 °C.¹⁸² Unlike the zinc and cadmium reagents, the copper reagents have versatile chemical reactivity. The pregenerated copper reagents couple with aryl iodides to give perfluoroalkyl aryl acetylenes.¹⁸²



Reaction of the alkynylcopper reagents with perfluorovinyl iodides afforded the perfluoroenynes. The stereochemistry of the vinyl iodides was preserved in the enynes.¹⁸²

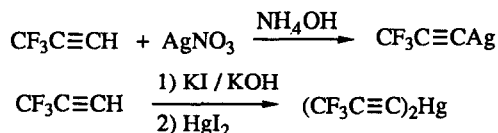


Coupling reaction of these copper reagents with the corresponding 1-iodoperfluoroalkynes gave the perfluorodiyne. However, an attempt to prepare an unsymmetrical diyne by reaction of iodoperfluoroalkyne with a different perfluoroalkynylcopper resulted in a mixture of diynes. This result is indicative of an exchange reaction occurring under the reaction conditions between the alkynyl iodide and alkynyl copper species.



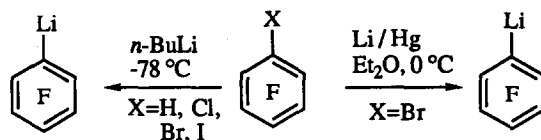
Pentafluorophenylethynylcopper has been prepared by reaction of pentafluorophenylacetylene with cuprous salts. Treatment of the copper reagent with iodobenzene in refluxing pyridine gave phenylethynylpentafluorobenzene in 74% yield.¹⁸⁴ In the presence of cuprous chloride oxidative coupling of pentafluorophenylacetylene was readily achieved by bubbling air to afford perfluorodiphenylbutadiyne in excellent yield presumably through the intermediacy of pentafluorophenylethynylcopper.

Trifluoropropynylsilver is obtained when trifluoropropyne reacts with silver nitrate in ammonium hydroxide solution. Trifluoropropynylmercury is synthesized by reaction of trifluoropropyne with potassium iodide and mercuric iodide in alkaline solution.¹⁸³

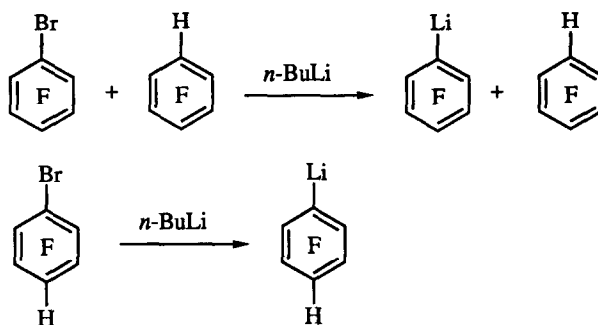


11. Perfluoroarylithium Reagents²

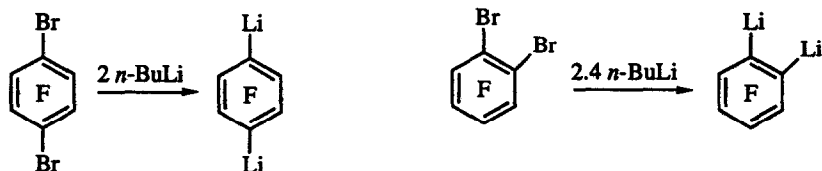
Pentafluorophenyllithium can be readily prepared by direct reaction of pentafluorophenyl halides with lithium amalgam in ether or THF.^{185, 186} Alternatively, lithium-hydrogen¹⁸⁷ and lithium-halogen exchange reactions of alkyllithiums with pentafluorobenzene or pentafluorophenyl halides provide routes to



pentafluorophenyllithium.^{188, 189, 190, 191} These facile exchange reactions have been carried out in high yields in a variety of solvents at -70 to -78 °C. Ether, THF and a mixture of ether and THF are the most widely used solvents utilized in the preparation of lithium reagents. Hexane and pentane are comparable, even though the reagent precipitates from hexane solution as a white solid.¹⁹² The rate of exchange reaction decreases in the order THF > ether > hexane.¹⁸⁷ Lithium-bromine exchange takes place in preference to lithium-hydrogen exchange. This has been demonstrated by both intramolecular and intermolecular competition reactions.¹⁹³

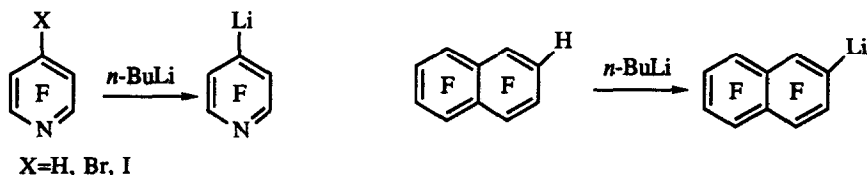


Dimetallation of 1,4-dibromo- or 1,4-dihydrotetrafluorobenzene with two equivalents of *n*-butyllithium in THF/hexane or ether/hexane yields 1,4-dilithiotetrafluorobenzene within a few minutes. However, attempts to prepare 1,2-dilithiotetrafluorobenzene under similar conditions proved to be difficult.^{187, 193} Reaction of two equivalents of *n*-butyllithium with 1,2-dibromotetrafluorobenzene gave a mixture of mono and bis lithium reagents as indicated by hydrolysis of the reaction mixture. When 2.4 equivalents of *n*-butyllithium were used, the 1,2-dibromide was completely converted to the corresponding bis-lithium reagent in 95-97% yields.¹⁹⁴

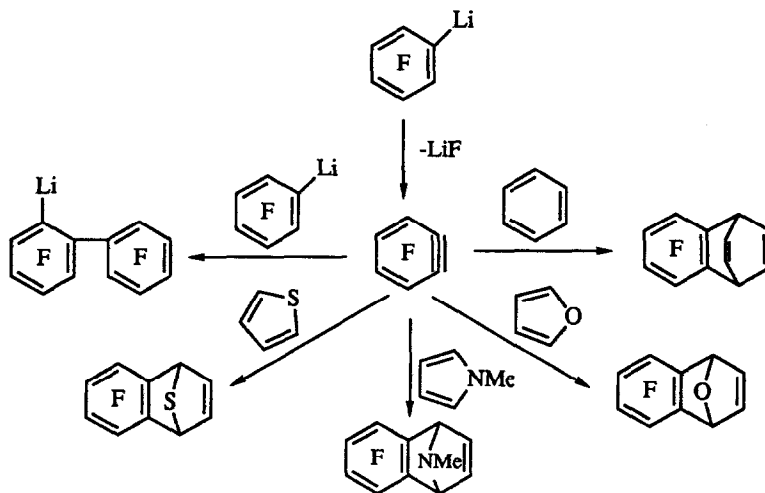


Pentafluorophenyllithium is also obtained by reaction of pentafluorophenylmercury^{195, 196} or titanium reagents with alkyllithium reagents.¹⁹⁷

Similarly, tetrafluoropyridyl and heptafluoronaphthyl lithium reagents can be prepared by either lithium-hydrogen or lithium-halogen exchange reactions.^{198, 199, 200, 201, 202}

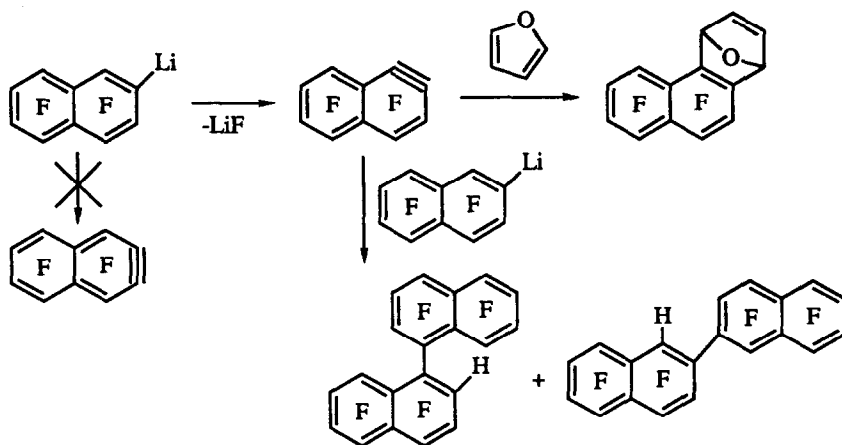


Pentafluorophenyllithium is thermally unstable and undergoes 42% decomposition after 24 hours at $-10\text{ }^{\circ}\text{C}$.¹⁸⁵ Thus, this reagent should be prepared at low temperature, preferably $-78\text{ }^{\circ}\text{C}$ by an exchange reaction. The thermal decomposition of pentafluorophenyllithium proceeds by β -elimination of lithium fluoride to give tetrafluorobenzynes which is then attacked by the lithium reagent to form perfluorobiphenyl or triphenyl derivatives. In the presence of dienes such as furan, thiophene, 1-methylpyrrole and benzenes, the benzyne intermediate is trapped to give Diels-Alder adducts.^{185, 188, 189, 203}

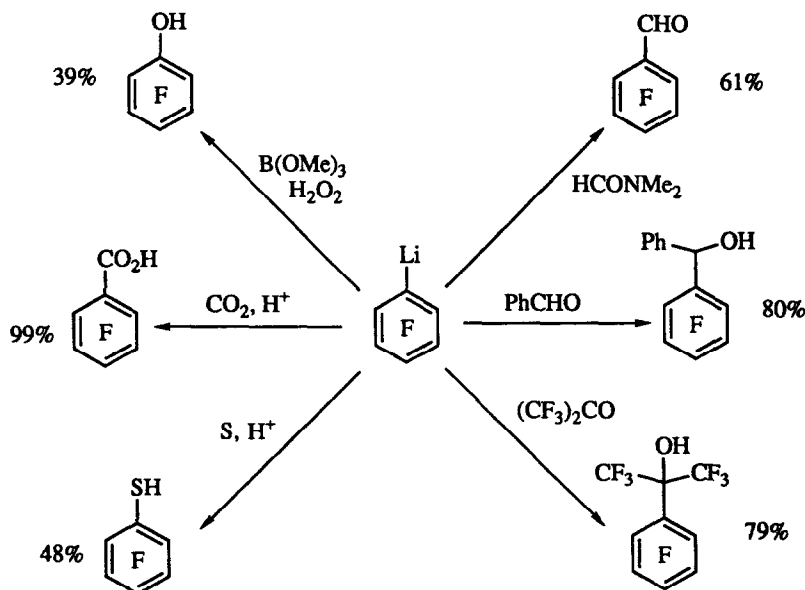


However, when 4-lithiotetrafluoropyridine is allowed to thermally decompose only polymeric products are observed even in the presence of furan.²⁰⁴ This result implies that the pyridine system favors nucleophilic

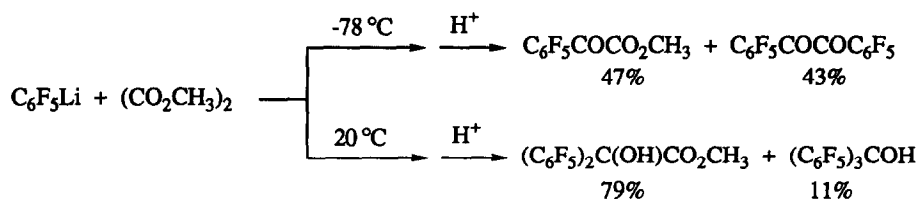
attack rather than intramolecular lithium fluoride elimination and no benzyne-type intermediate is formed. Interestingly, when 2-lithioheptafluoronaphthalene is warmed to room temperature, only 1,2-naphthalene and not its 2,3-isomer is observed. The 1,2-naphthalene can be readily trapped by either furan to give a Diels-Alder adduct or attacked by the remaining lithium reagent to form dimers.^{201, 202}



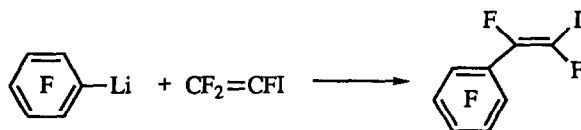
Oxidative coupling reaction of pentafluorophenyllithium occurs after treatment with TiCl_4 to provide perfluorobiphenyl in good yield.^{190, 205} Pentafluorophenyllithium reacts readily with electrophiles such as water and halogens to give pentafluorobenzene and pentafluorophenyl halides, respectively.¹⁸⁹ Pentafluorobenzoic acid is obtained in quantitative yield after treatment of the lithium reagent with carbon dioxide followed by protonolysis.¹⁸⁷ Pentafluorophenyllithium also reacts with sulfur^{206, 207} to yield, after



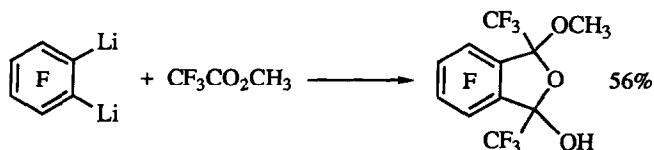
protonolysis, pentafluorothiophenol. Pentafluorophenol can be obtained when pentafluorophenyllithium reacts with trimethylborate and hydrogen peroxide.²⁰⁸ The lithium reagent reacts with a variety of carbonyl compounds to give carbinols. For example, treatment of the lithium reagent with benzaldehyde¹⁸⁵ or hexafluoroacetone²⁰⁹ gives pentafluorophenyl alcohols. With DMF, pentafluorobenzaldehyde is obtained.¹⁸⁷ Reaction of the reagent with α,β -diketones or dimethyl carbonate produces α -hydroxyketones and bis(pentafluorophenyl) ketones respectively.²¹⁰ When pentafluorophenyllithium reacts with dimethyl or di-*tert*-butyl oxalate the products obtained depend upon the reaction temperature. At -78°C , α,β -diketone and α -ketoester are obtained, whereas an α -hydroxyester and an alcohol are formed when the reaction is carried out at 20°C . The latter product presumably formed *via* methoxide-induced rearrangement of the α,β -diketone.²¹¹



Pentafluorophenyllithium gives fluorinated alkenes upon reaction with fluorinated alkenes.¹⁸⁹ Chambers and Taylor reported the nucleophilic substitution reactions of $\text{C}_6\text{F}_5\text{Li}$ with perfluorocyclobutene oligomers.²¹² They discovered that when $\text{C}_6\text{F}_5\text{Li}$ is added to the perfluorocyclobutene derivative, vinylic substitution occurred to give pentafluorophenyl-substituted cyclobutene derivatives. The product reacted further with excess lithium reagent to afford the perfluorobiphenyl-substituted product. The lithium reagent also underwent reaction with iodotrifluoroethylene to provide the addition / elimination product rather than the displacement product.²¹³

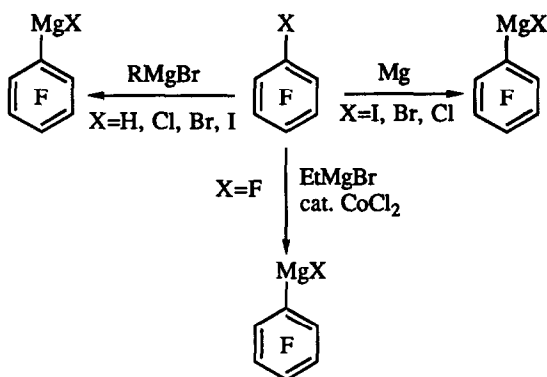


Dicarboxylation of 1,4-dilithiotetrafluorobenzene with carbon dioxide affords the corresponding diacid in 92% yield.¹⁹³ 1,2-Dilithiotetrafluorobenzene reacts with methyl trifluoroacetate to give a mixed ketal / hemiketal product.²¹⁴

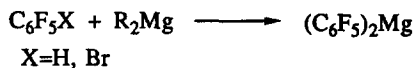


12. Perfluoroarylmagnesium Reagents

Pentafluorophenylmagnesium halides can be prepared either by direct reaction of magnesium with pentafluorophenyl chloride, bromide or iodide in ethereal solvents or by exchange reaction of alkylmagnesium halides with hydro-, bromo- and chloropentafluorobenzenes.^{187,192,215,216,217,218,219} In the presence of cobalt dichloride, hexafluorobenzene has been converted to pentafluorophenylmagnesium bromide by reaction with ethylmagnesium bromide.²²⁰

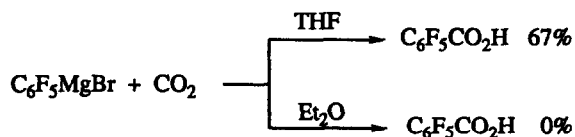


Bis(pentafluorophenyl)magnesium has been synthesized from reaction of dialkylmagnesium with either pentafluorobenzene or bromopentafluorobenzene.²¹⁵

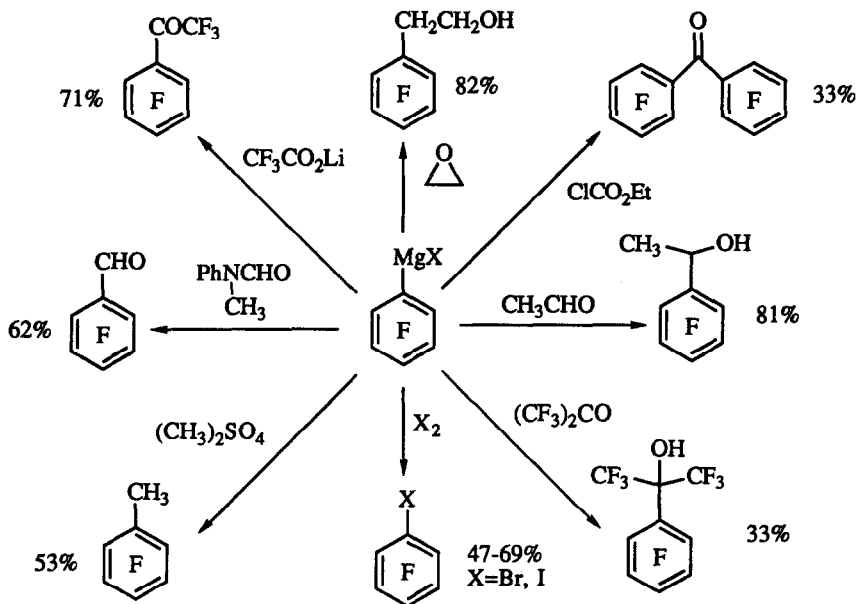


Mercury-magnesium exchange of pentafluorophenylmercurials and bis(organo)-magnesiums also gave bis(pentafluorophenyl)magnesium.²²¹ 4-Tetrafluoropyridyl and 1- and 2-heptafluoronaphthyl Grignard reagents have been prepared by the reaction of magnesium with the corresponding halides in THF.^{197, 217}

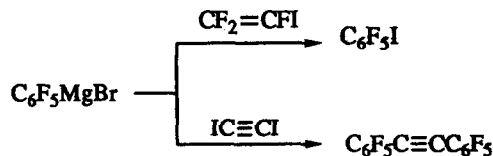
The pentafluorophenylmagnesium reagents exhibit greater thermal stability than the corresponding lithium reagents. Thus, the Grignard reagents have been utilized more widely in the synthesis of fluorinated aromatics. However, the stability and reactivity of the Grignard reagents are very dependent upon the solvent. For example, carboxylation of pentafluorophenylmagnesium halides in THF gives the corresponding acid in 66% yield while none of the desired product is observed in ether.²¹⁷ On the other hand, pentafluorophenylmagnesium bromide is stable in refluxing ether, but decomposition occurs in refluxing THF to produce polyphenylene.²²² The warming of pentafluorophenylmagnesium halides in the presence of dienes or aromatics affords Diels-Alder adducts of tetrafluorobenzene in a reaction analogous to that of pentafluorophenyllithium.²²³



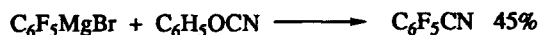
Pentafluorophenyl Grignard reagents react with a variety of electrophilic substrates. Reaction with halogens^{186, 217} or ethylene oxide²²⁴ gives pentafluorophenyl halides and 2-pentafluorophenylethanol, respectively. When aldehydes and ketones are used as substrates, pentafluorophenylcarbinols are obtained in good yields. The Grignard reagent gives pentafluorobenzaldehyde with ethyl formate or *N*-methyl-*N*-phenylformamide.²¹⁷ Although reaction of the Grignard reagents with acid chlorides gives pentafluorophenyl ketones significant amounts of carbinols are usually formed as byproducts. The replacement of acyl chlorides by metallic carboxylates improves the yields of desired ketones. Octafluoroacetophenone has been prepared in high yield from the Grignard reagent and lithium trifluoroacetate.²²⁵ Reactions with electrophiles such as ethyl chloroformate,²¹⁷ acetaldehyde,^{226, 227} hexafluoroacetone,²⁰⁹ and dimethyl sulfate²²⁸ give the expected products.



Unlike pentafluorophenyllithium, the Grignard reagent reacts with trifluorovinyl iodide to afford the exchange product, iodopentafluorobenzene, rather than the substitution product, pentafluorophenyl-trifluoroethylene.²²⁷ Reaction with diiodoacetylene yields bis(pentafluorophenyl)acetylene.²²⁹

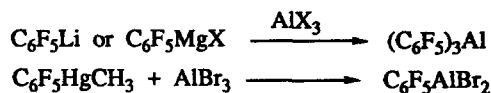


Treatment of pentafluorophenylmagnesium bromide with phenyl cyanate gave pentafluorophenyl nitrile in 45% yield.⁷⁵

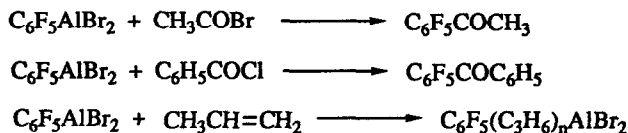


13. Perfluoroarylaluminum Reagents

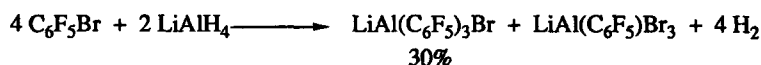
When aluminum trihalides are treated with pentafluorophenyllithium or Grignard reagents tris(pentafluorophenyl)aluminum is formed as a solvent complex.²³⁰ Although hexane, benzene and toluene are also used as solvents ether is necessary as a cosolvent in order to isolate pure product. Pentafluorophenylaluminum halides can also be prepared readily by exchange reaction of pentafluorophenylmercurials with aluminum halides.²³¹



Although pentafluorophenylaluminum reagents exhibit good thermal stability, they are extremely air and moisture sensitive. They will spontaneously ignite in air and explode during uncontrolled hydrolysis. Pentafluorophenylaluminum reagents have been shown to be strong Lewis acids and form complexes with Lewis base solvents. They react with acid halides to give pentafluorophenyl ketones in high yields.²³¹ Insertion of alkenes into the aluminum reagents leads to a pentafluorophenyl-substituted polymer.²³²



Reaction of lithium aluminum hydride with bromopentafluorobenzene at -78°C in THF gave lithium tris(pentafluorophenyl)bromoaluminate.²³³

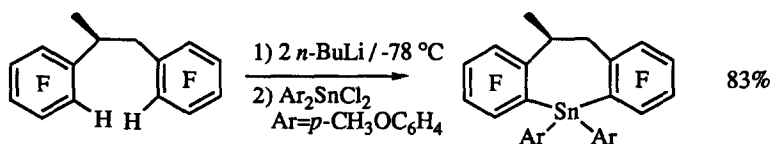


14. Perfluoroaryltin and Lead Reagents

Direct preparation of tetrakis(pentafluorophenyl)tin has been achieved by reaction of tin metal with iodopentafluorobenzene at 200 °C.²³⁴ Exchange reactions provide alternative routes to the tin reagents under more mild conditions. Pentafluorophenyllithium²³⁵ and Grignard^{236, 237, 238, 239} reagents are treated with tin chloride to produce the corresponding tin reagents in good yields. When excess tin tetrachloride is used as a substrate the Grignard reagent gives pentafluorophenyltin halides. Reaction of bis(pentafluorophenyl)mercury with tin metal in a sealed tube has been utilized to prepare tetrakis(pentafluorophenyl)tin.²⁴⁰

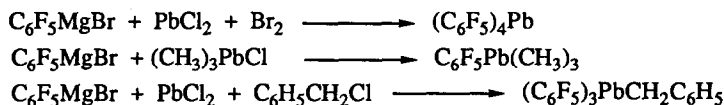


Fluorinated aromatic rings have recently been employed to enhance the Lewis acidity of cyclic organotin compounds, prepared by trapping of the requisite dilithio substrate with an organotin dihalide.²⁴¹



Diphenyl(octafluorobiphenylene) stannane has similarly been prepared from 2,2'-dilithiooctafluorobiphenyl and diphenyltin dichloride.²⁴²

Pentafluorophenyllithium reacts with lead tetraacetate to yield tetrakis(pentafluorophenyl)lead.²³⁵ Treatment of the pentafluorophenyl Grignard reagent with lead dichloride in the presence of bromine also gave the lead reagent.²⁴³ Reaction of the Grignard reagent with lead dichloride and benzyl chloride afforded tris(pentafluorophenyl)benzyllead in good yield.²⁴³ In the latter reaction $(\text{C}_6\text{F}_5)_3\text{PbMgBr}$ may be an intermediate. The decarboxylation of triphenyllead pentafluorobenzoate also gives triphenyl-pentafluorophenyllead.²

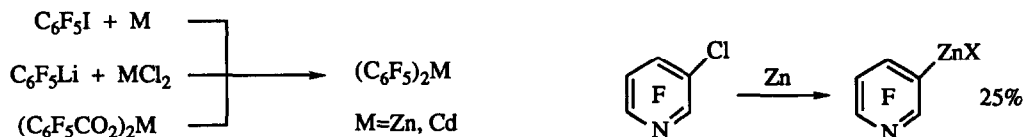


Tetrakis(pentafluorophenyl)tin and lead are very thermally stable and do not react with water,²⁴⁴ chlorine or bromine.² However, with dry hydrogen chloride tetrakis(pentafluorophenyl)tin and trimethyl-pentafluorophenyllead give pentafluorobenzene.²⁴⁴ The tin and lead compounds have limited synthetic applications due to their low reactivity and high stability.

15. Perfluoroarylzinc and Cadmium Reagents

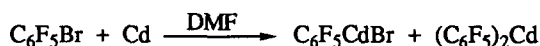
Bis(pentafluorophenyl)zinc and cadmium have been prepared by direct reaction of iodopentafluorobenzene with zinc or cadmium at 200 °C,² by metathesis of pentafluorophenyllithium or

Grignard reagents with zinc chloride or cadmium chloride,^{245, 246, 247} and by decarboxylation of zinc or cadmium bis(pentafluorobenzoate),^{246, 248} Tetrafluoropyridyl zinc reagents have also been prepared by Satori and Platonov.²⁴⁹

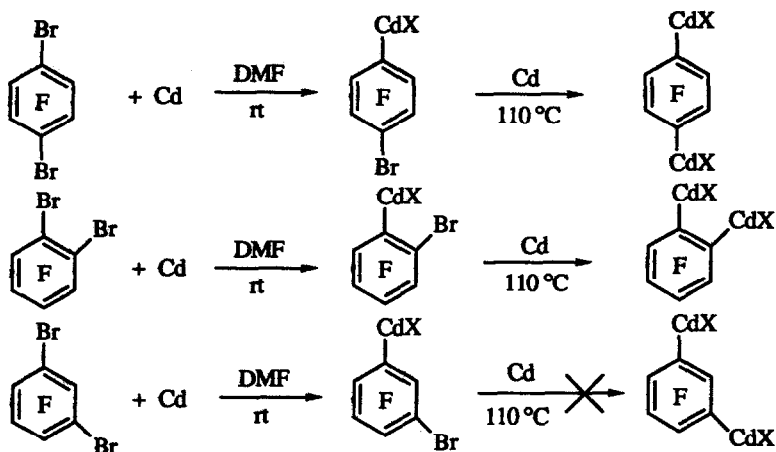


In 1973, Evans reported that zinc reacted directly with iodopentafluorobenzene in a variety of solvents such as THF, ether, glymes, DMF, DMAC and DMSO to give pentafluorophenylzinc products.²⁴⁵ Bromopentafluorobenzene undergoes the analogous reaction. The resultant mixture consisted of bis(pentafluorophenyl)zinc and pentafluorophenylzinc halide, as determined by ¹⁹F NMR spectroscopy. Addition of a zinc iodide solution decreased the relative intensity of the high field triplet (*para*-fluorine resonance) which could be assigned to bis(pentafluorophenyl)zinc according to the Schlenk equilibrium. Similarly the pentafluorophenylcadmium reagent could be prepared from the reaction of iodopentafluorobenzene with cadmium.²⁴⁵ Naumann also reported that bis(pentafluorophenyl)zinc or cadmium could be prepared in quantitative yield from the reaction of iodopentafluorobenzene with Me₂M (M=Zn or Cd) in glyme.²⁵⁰

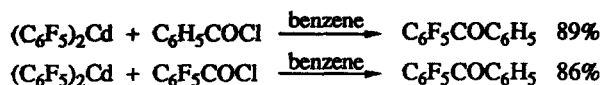
More recently, Burton and co-workers found that reaction of bromopentafluorobenzene with acid-washed cadmium under mild conditions gave pentafluorophenylcadmium reagents in high yields.²⁵¹ The reaction was exothermic and generally was complete within a few hours. A mixture of mono- and bis-pentafluorophenylcadmium reagents were obtained which were identified by ¹⁹F NMR and ¹¹³Cd NMR. This method is preferred because of the commercial availability and lower cost of bromopentafluorobenzene.



When dibromotetrafluorobenzenes were reacted with excess cadmium in DMF, the formation of mono- and bis-cadmium reagents was observed depending upon the reaction conditions.²⁵² Mono-cadmium reagents only were the products in high yields at room temperature to 60 °C. However more forcing conditions gave the bis-cadmium reagents. When the reaction was conducted at 100 to 110 °C for two to three days, 1,4-dibromotetrafluorobenzene afforded the 1,4-bis-cadmium reagent in 90% yield while 1,2-dibromotetrafluorobenzene gave the corresponding bis-cadmium reagent in 75% yield. Although reaction of 1,3-dibromotetrafluorobenzene with cadmium in DMF produces the mono-cadmium reagent in quantitative yield attempts to prepare the bis-cadmium reagent failed even after prolonged heating at 110 to 120 °C for four days.



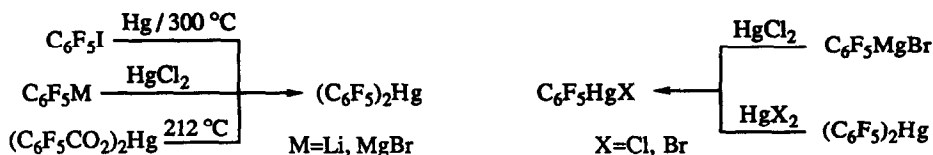
Pentafluorophenylzinc and cadmium reagents have high thermal stability. Bis(pentafluorophenyl)zinc and cadmium form 1:1 complexes with a variety of ligands such as 2,2'-bipyridyl.^{248, 253} Although no functionalization reactions of the pentafluorophenylzinc reagent have been investigated, acylation of pentafluorophenylcadmium reagents with acetyl and benzoyl chlorides in benzene gives the expected ketones.²⁴⁸ However when pentafluorobenzoyl chloride was used as a substrate pentafluorobenzophenone rather than decafluorobenzophenone formed. The explanation for this unexpected transformation is that bis(pentafluorophenyl)cadmium behaves as a strong Lewis acid due to the high electronegativity of the pentafluorophenyl group which enables it to catalyze a Friedel-Crafts arylation reaction.



Allylpentafluorobenzene is obtained in good yield by reaction of the pentafluorophenylcadmium reagent with allyl bromide in DMF.²⁵⁴

16. Perfluoroarylmercury Reagents

Bis(pentafluorophenyl)mercury can be readily prepared by direct reaction of bromo- or iodopentafluorobenzene with mercury at elevated temperature,²⁵⁵ by photolysis of pentafluorophenyl(trimethylsilyl)mercury,²⁵⁵ by exchange reactions of pentafluorophenyllithium,¹⁹⁰ Grignard,²⁵⁶ thallium²⁵⁷ and titanium²⁰⁵ reagents with mercury halides, by decarboxylation of mercury bis(pentafluorobenzoate)²⁵⁸ and by sulfur dioxide elimination from lithium polyfluorobenzene sulfonates in the presence of mercury salts.²⁵⁸ Treatment of mercury halides with a 1:1 mol ratio of pentafluorophenyl Grignard reagent gives pentafluorophenylmercury halides¹⁹⁰ although they are most readily obtained by an exchange reaction of bis(pentafluorophenyl)mercury with mercury halides.^{256, 259}

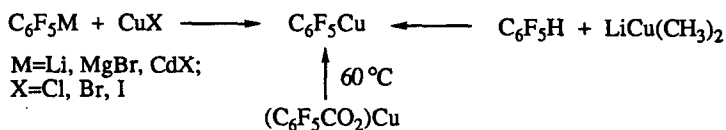


Bis(pentafluorophenyl)mercury is extremely stable. No decomposition has been observed either after heating for five hours at 250 °C or after recrystallization from concentrated sulfuric acid. However, the mercury reagent reacts slowly with bromine in carbon tetrachloride²⁵⁶ or with iodide in aqueous ethanol.²⁶⁰ Nucleophilic substitutions with hydroxide, methoxide and hydrazine occur only at the *para*-position of the pentafluorophenyl ring of the mercury reagent.¹⁹⁵ Treatment of bis(pentafluorophenyl)mercury with alkylolithiums gives pentafluorophenyllithium in high yields.¹⁹⁵ Because of its remarkable stability bis(pentafluorophenyl)mercury has not been used in organic synthesis. Cleavage of the carbon-mercury bond could be affected with lithium aluminum hydride to give pentafluorobenzene.¹⁹⁵ Perhaps the mercurial could find application as a protecting group in organic synthesis.

Pentafluorophenyl derivatives of elements such as sulfur, selenium, tellurium, germanium and tin have been prepared by heating a mixture of pentafluorophenylmercury derivatives and the corresponding element.^{240, 261} Bis(pentafluorophenyl)mercury also exhibits Lewis acid characteristics and forms a variety of complexes with neutral ligands.

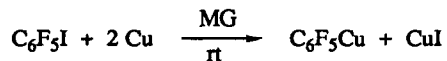
17. Perfluorophenylcopper Reagents

Although the reaction of pentafluorophenyl bromide with copper gives perfluorobiphenyl, no pentafluorophenylcopper intermediate has been detected. Pentafluorophenylcopper was first prepared by metathesis of pentafluorophenylmagnesium halide with cuprous halides in dioxane.^{262, 263} The copper reagent has also been synthesized by reaction of pentafluorophenyllithium with cuprous chloride^{264, 265} or by the action of lithium dimethylcopper on pentafluorobenzene or iodopentafluorobenzene in ethereal solvents at low temperature.^{264, 265} Exchange reaction of pentafluorophenylcadmium reagent with cuprous halides also gives pentafluorophenylcopper in quantitative yield in DMF at room temperature.^{266, 267} Decarboxylation of cuprous pentafluorobenzoate in quinoline at 60 °C produces pentafluorophenylcopper in 72% yield.²⁶⁸

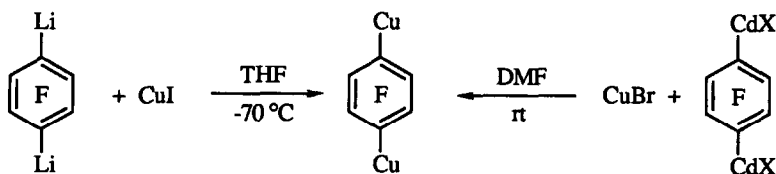


More recently, Rieke and co-workers reported that pentafluorophenylcopper could be prepared by the reaction of iodopentafluorobenzene with highly activated copper generated by the reduction of cuprous iodide with potassium in the presence of 10% naphthalene. The activated copper reacted with iodopentafluorobenzene in 30 minutes at room temperature in monoglyme to form the copper reagent. Although it was difficult to isolate and purify the copper reagent, its chemistry was similar to that of pure pentafluorophenylcopper. It yielded decafluorobiphenyl upon air oxidation or thermal decomposition and pentafluorobenzene by

hydrolysis. The Ullmann coupling reaction took place to give decafluorobiphenyl in 83% yield when the reaction was carried out for extended times or in refluxing monoglyme. This result implies that Rieke's copper is sufficiently active to generate pentafluorophenylcopper at a temperature which is low enough to avoid Ullmann coupling.^{269, 270, 271}

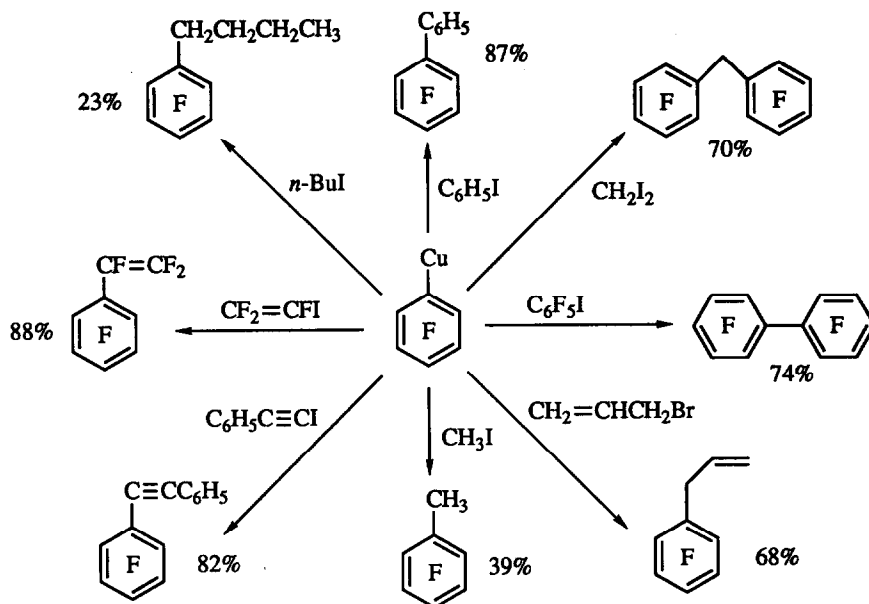


Although preparation of 1,4-dicuprotetrafluorobenzene has been achieved from the 1,4-dilithium reagent in THF at -70°C , no spectroscopic data have been reported.²⁷² Recently, bis-cuprotetrafluorobenzene was conveniently obtained from the 1,4-dicadmium reagent and cuprous bromide in DMF at room temperature.²⁵² However, only decomposition products were observed upon metathesis of 1,2-dicadmiumtetrafluorobenzene with cuprous bromide at room temperature.

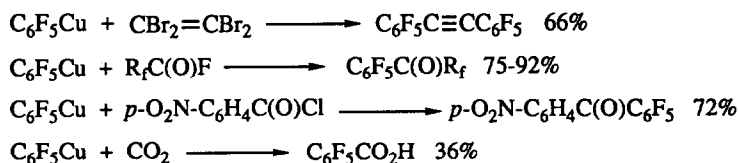


Pentafluorophenylcopper is much more thermally stable than the corresponding hydrogen analog. The fluorinated copper reagent can be isolated as colorless 1:1 and 2:1 dioxane complexes, which are freed of dioxane by heating at 130°C in *vacuo*.²⁶² It decomposes above 200°C to form decafluorobiphenyl and copper metal and is hydrolyzed and oxidized slowly in moist air. The copper reagent exists as a tetramer in the vapor state and in benzene solution and is soluble in most aprotic solvents.²⁷³

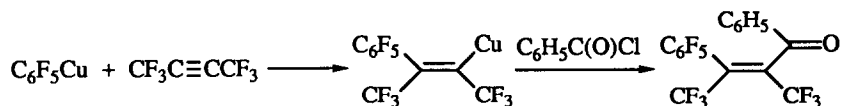
Pentafluorophenylcopper exhibits high reactivity towards organic substrates, and reacts with fluorinated or non-fluorinated aryl iodides,^{262, 263} fluorinated vinyl iodides,^{263, 274, 275} alkynyl bromides and iodides,^{276, 277} allyl halides²⁶² and methyl iodide²⁶² to afford the corresponding coupled products in good yields. Methylene iodide and pentafluorophenylcopper give bis(pentafluorophenyl)methane in 70% yield.²⁶⁵ However, longer chain alkyl halides such as butyl iodide give only a low yield of the desired product.²⁶⁵



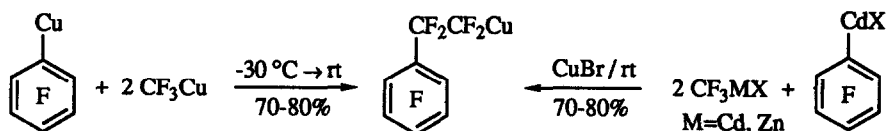
Reaction of tetrabromoethylene and pentafluorophenylcopper gave no tetrakis(pentafluorophenyl)ethene. Instead bis(pentafluorophenyl)acetylene was obtained in 66% yield.^{276, 277} Unlike pentafluorophenyl Grignard reagents pentafluorophenylcopper reacts with primary or secondary perfluoroalkyl acid fluorides²⁷⁸ or *para*-nitrobenzoyl chloride²⁶² to give the ketones in excellent yields with carbinol byproducts from competing secondary reactions. Carboxylation of pentafluorophenylcopper with carbon dioxide in DMAC gave pentafluorobenzoic acid in 36% yield.²⁶³ None of the acid was observed when the copper reagent was treated with carbon dioxide in THF under similar conditions.



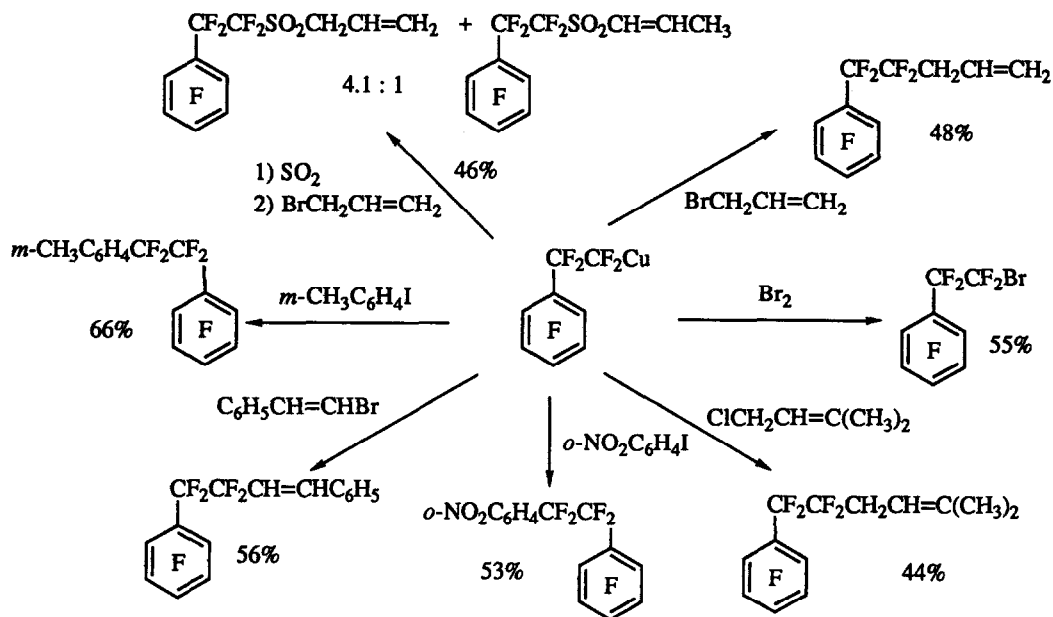
Pentafluorophenylcopper readily adds to hexafluoro-2-butyne to form a perfluorovinylcopper reagent, which can be quenched by electrophiles such as benzoyl chloride and methyl iodide to give isolable products.^{266,267} ¹⁹F NMR analysis of the final products demonstrated that a stereospecific *syn* addition had occurred.



A remarkable double difluoromethylene insertion into the carbon-copper bond of pentafluorophenylcopper to give $C_6F_5CF_2CF_2Cu$ in high yield was observed when pentafluorophenylcopper was treated with CF_3Cu in DMF at $-30\text{ }^\circ\text{C}$ to rt.¹⁶³ This insertion product was also observed after treatment

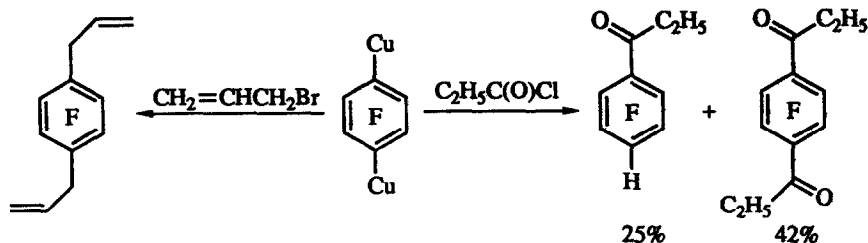


of C_6F_5CdX with CF_3MX ($M=\text{Zn}$ or Cd) in the presence of CuX . Presumably, $C_6F_5CF_2Cu$ was an intermediate in the latter reaction. The copper reagent, $C_6F_5CF_2CF_2Cu$, readily underwent a variety of functionalization reactions.¹⁶³



Riecke's pentafluorophenylcopper reagent also underwent coupling reactions with allyl, benzyl and aryl halides.^{269, 270, 271} With benzoyl chloride the corresponding ketone was obtained in low yield.

Allylation of 1,4-dicuprotetrafluorobenzene with allyl bromide is facile and provides the bis-allylated product in 79% yield. When the bis-copper reagent was treated with acid chlorides an exothermic reaction occurred and the mono- and bis-acylated products were formed.²⁵²



Pentafluorophenylcopper has been utilized in natural product syntheses to promote decarboxylation,²⁷⁹ condensation,²⁸⁰ and ring-expansion reactions.²⁸¹

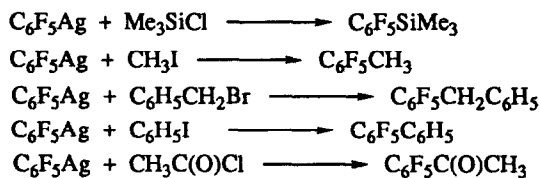
18. Perfluorophenylsilver Reagents

Pentafluorophenylsilver has been prepared by metathesis of pentafluorophenyllithium with silver acetate in ether and by exchange reaction of bromopentafluorobenzene with heptafluoroisopropylsilver in acetonitrile.²⁸²



Pentafluorophenylsilver is much more stable than phenylsilver and decomposed slowly to form perfluorobiphenyl at 150 °C. Decomposition of the silver reagent in solution can be promoted by heat, light, moisture or reaction with oxygen.

The functionalization of pentafluorophenylsilver smoothly occurs to give the corresponding pentafluorophenyl-substituted products.²⁸² The reaction of the silver reagent with trimethylsilyl chloride gave pentafluorophenyltrimethylsilane. When methyl iodide and benzyl bromide were used as substrates pentafluorotoluene and 2,3,4,5,6-pentafluorodiphenylmethane were obtained respectively. Pentafluorophenylsilver also coupled with iodobenzene and acetyl chloride. However, reaction of the silver reagent with heptafluoro-2-iodo-2-butene gave only iodopentafluorobenzene and vinylsilver reagent, but not the coupled product.



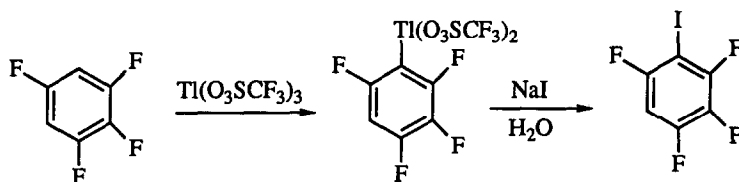
Pentafluorophenylsilver also undergoes metathesis reactions. Treatment of the silver reagent with zinc iodide, cuprous chloride, or mercuric bromide in ether at room temperature afforded the corresponding pentafluorophenylmetallic reagents.²⁸²

Smith and Massey reported the preparation of lithium bis(pentafluorophenyl)silver by the slow addition of cooled silver chloride to an ether solution of pentafluorophenyllithium at $-78\text{ }^{\circ}\text{C}$.²⁸³ Filtration and evaporation of the solvent gave moisture-sensitive $\text{LiAg}(\text{C}_6\text{F}_5)_2$, which was stable to $80\text{ }^{\circ}\text{C}$. When $\text{LiAg}(\text{C}_6\text{F}_5)_2$ was decomposed thermally in a sealed and evacuated tube, decafluorobiphenyl was obtained with small amounts of *ortho*-linked polyfluoropolyphenyls. The result suggests that tetrafluorobenzene may be one of the decomposition intermediates. Hydrolysis of $\text{LiAg}(\text{C}_6\text{F}_5)_2$ with dilute acid produced pentafluorobenzene. When the salt was exposed to small quantities of water, either in the form of moist air or wet solvents, $\text{C}_6\text{F}_5\text{Ag}$ was formed as a white solid. $\text{LiAg}(\text{C}_6\text{F}_5)_2$ also underwent a metathesis reaction with mercuric chloride to give bis(pentafluorophenyl)mercury.

Silver trifluoroacetate reacted with an excess of pentafluorophenyllithium to give solutions which, after addition of tetrabutylammonium trifluoroacetate, afforded $\text{Bu}_4\text{N}[\text{Ag}(\text{C}_6\text{F}_5)_2]$. Treatment of $\text{Bu}_4\text{N}[\text{Ag}(\text{C}_6\text{F}_5)_2]$ with AgClO_4 in ether produced AgC_6F_5 while $(\text{CF}_3\text{CO}_2)\text{Ag}$ or AgNO_3 gave the new complex, $\text{Bu}_4\text{N}\{\text{Ag}(\text{C}_6\text{F}_5)_2\text{X}\}$.²⁸⁴ Analogous pentafluorophenylgold complexes have also been reported.^{285,286}

19. Miscellaneous Perfluorophenyl Organometallics

The reaction of pentafluorophenyl magnesium bromide with thallium trichloride in hydrocarbon solvent gave a mixture of tris(pentafluorophenyl)thallium and bis(pentafluorophenyl)thallium bromide.^{230, 287} However, when ether was used as a solvent, only tris (pentafluorophenyl thallium) was formed.^{257, 288} Direct metallation of polyfluorobenzenes with thallic triflate produced the corresponding polyfluorophenylthallic compounds which can react with sodium iodide to give polyfluoroiodobenzene.^{289, 290}

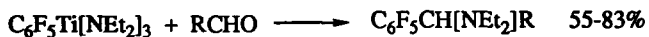


The pentafluorophenylthallium compounds exhibited Lewis acid properties. Bis(pentafluorophenyl)thallium halide formed a variety of four and five coordinate derivatives of the bis(pentafluorophenyl)thallium halides with neutral ligands.^{290, 291}

Dicyclopentadienyl-pentafluorophenyltitanium compounds have been prepared by similar methods. Treatment of dicyclopentadienyltitanium dichloride with pentafluorophenyllithium or Grignard reagents gave a mixture of monopentafluorophenyltitanium and bis(pentafluorophenyl)titanium compounds.²⁹²

Reaction of dicyclopentadienyltitanium dichloride with pentafluorophenylmagnesium bromide gave racemic $\text{Cp}_2\text{TiClC}_6\text{F}_5$ which was treated with the sodium salt of (-)-(S)-2-phenyl-1-propanol at $-60\text{ }^{\circ}\text{C}$ in THF to give the corresponding diastereomers. This diastereomeric mixture was readily separated by preparative thin layer chromatography. Reaction with HCl in benzene solution afforded the two enantiomeric forms of the pentafluorophenyltitanium compound.²⁹³

Pentafluorophenyltris(diethylamido)titanium was prepared by the reaction of pentafluorophenyl Grignard reagent with chlorotris(diethylamido)titanium.²⁹⁴ The titanium reagent underwent pentafluorophenyl transfer reactions. Treatment with aldehydes resulted in pentafluorophenylamino derivatives.



Polyfluorophenyl halides readily undergo oxidative addition with metal vapors to form non-solvated polyfluorophenyl metallic halides.²⁹⁵ Pentafluorophenyl halides reacted with Rieke's nickel, cobalt or iron to give $(\text{C}_6\text{F}_5)_2\text{M}$ ($\text{M}=\text{Ni}, \text{Co}, \text{Fe}$), which could be isolated in good yields as ligand complexes.^{296, 297} Rieke's nickel could also be utilized to promote the coupling reaction of iodopentafluorobenzene with acid halides, presumably *via* the intermediacy of pentafluorophenylnickel.²⁹⁷

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List of Abbreviations:

Bz - Benzyl

C_p - Cyclopentadienyl

DAST - Diethylaminosulfur Trifluoride

dba - Dibenzylideneacetone [PhCH=CHCOCH=CHPh]

DIBAL - H - Diisobutylaluminum Hydride

DMAC - *N,N*-Dimethylacetamide

DMAP - 4-(Dimethylamino) pyridine

DMF - Dimethylformamide

DMSO - Dimethyl sulfoxide

Et₂O - Diethyl Ether

HMPA - Hexamethylphosphoramide (Hexamethylphosphoric triamide)

hν - photolysis

LDA - Lithium Diisopropylamide

MCPBA - *m*-Chloroperoxybenzoic acid

MEM - (2-methoxyethoxymethyl)methyl

MOM - Methoxymethyl

NBS - *N*-Bromosuccinimide

Ph - Phenyl

R_f - Perfluoroalkyl group

TASF - Tris (dimethylamino) sulfonium difluorotrimethylsilicate

Tf - Trifluoromethanesulfonyl

TG - Triglyme (trimethylene glycol dimethylether)

THF - Tetrahydrofuran

TMEDA - *N,N,N,N*-Tetramethyl-1,2-ethylenediamine

TMS - Trimethylsilyl

TMSCl - Trimethylsilyl Chloride

Ts - *p*-Toluenesulfonyl

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