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Room Temperature Preparation of Trifluoroethenylzinc Reagent by Metalation of the Readily Available Halocarbon HFC-134a and an Efficient, Economically Viable Synthesis of 1,2,2-Trifluorostyrenes

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Trifluoroethenylzinc reagent [$CF_2{=}CFZnX$] was generated from the readily available halocarbon HFC-134a by an in situ metalation−transmetalation procedure at temperatures near to room temperature (15−20 °C). By systematic standardization of the metalation experiments by manipulation of solvent, cosolvent, temperature, zinc salt, and the base, the trifluoroethenylzinc reagent was produced in 73% yield at 20 °C in THF medium. The palladium-catalyzed cross-coupling reaction of the trifluoroethenylzinc reagent with various aryl iodides was carried out under mild reaction conditions to produce 1,2,2-trifluorostyrenes in 59−86% isolated yields. The stability of the intermediate trifluoroethenyllithium reagent was compared at different temperatures and solvent systems. Experimental evidence for the mono-anion from HFC-134a (CF_3CHF^-) was obtained by the trapping of the mono-anion with zinc halide in THF/TMEDA medium. The structure and complexation of both the mono- and bis-trifluoroethenylzinc reagents with TMEDA and other ligands are discussed.

Introduction

1,2,2-Trifluorostyrene (TFS) is one of the important monomers among the fluorinated monomers capable of polymerization.[1] The polytrifluorostyrene (PTFS) or its copolymers with various fluorinated monomers have received recent attention as they are promising proton exchange membranes for fuel cell separators.[1a,2] Polytrifluorostyrene-coated silica as a packing material for column liquid chromatography,[3] its derivatized polymers as optical fibers,[4] and 4-chloro bromomethyl derivatives as an excellent alternative for Merrifield-type resin[5] have been explored in recent years.

A practical synthesis of 1,2,2-trifluorostyrene in good yield and purity has been a difficult task. Numerous methodologies have been developed to prepare this monomer in an efficient and cost-effective manner.[1a] The previously reported methods of Cohen[6] and Prober[7] involved many steps and suffered from low overall yields (<20%). Pyrolytic methods used for bulk production have the difficulty of low yield and the formation of many side products.[8] Formation of TFS through organometallic reagents has been the most impressive route. One of the earlier methods developed by Dixon[9] was promising, where reaction of an aryllithium reagent with tetrafluoroethylene (TFE) generated the 1,2,2-trifluorostyrene in low yields (30%). 1,2-Difluorostilbene formation was the major side reaction during this process. With an excess of the aryllithium, the diaryl- and triaryl-substituted products were favored.[10] Reactions of the phenyl derivatives of the lanthanides (Yb, Sm, Ce) with tetrafluoroethylene produced TFS in poor yield.[11] Synthesis of TFS through trifluoroethenylzinc and trifluoroethenyltin was developed in the past two decades. Sorokina et al. developed a palladium-catalyzed cross-coupling reaction of the trifluoroethenylzinc and trifloroethenyltin reagent with aryl iodides in DMF, HMPA medium.[12] The best method so far for TFS synthesis was developed from this

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SCHEME 1

$$CF_2{=}CFBr + Zn \xrightarrow[3h]{DMF,\ RT} [CF_2{=}CFZnBr] \xrightarrow[Pd(PPh_3)_4,\ 65\text{-}75\ ^{o}C]{DMF,\ ArI} ArCF{=}CF_2$$

SCHEME 2

$$CF_3CH_2F \xrightarrow{Base} [CF_3CHF]^- \xrightarrow[-F^-]{} CF_2{=}CHF \xrightarrow{Base} [CF_2{=}CF]^- \xrightarrow{E^+} CF_2{=}CFE$$

laboratory where the trifluoroethenylzinc reagent was generated from zinc and bromotrifluoroethylene (BTFE) in a variety of solvents (DMF, THF, TG).[13] The palladium-catalyzed cross coupling of the zinc reagent with aryl iodides generated 1,2,2-trifluorostyrenes in very good yields (Scheme 1). Since this reaction was performed under mild conditions the usual thermal cyclodimerization of TFS was absent. Also the stilbene formation observed in Dixon's method was eliminated. But the cost, the availability, and above all the environmental concern of BTFE remained as a major problem and thus made it difficult for commercial applications.

Normant and co-workers[14] generated a fluoroethenylzinc reagent via fluoroethenyllithium reagent from a fluorocarbon of the type $CF_2{=}CFY$, where Y = H, Cl, Br, I. Here the lithium reagent was generated by the reaction of the fluoroalkene with an alkyllithium at very low temperature, which was then converted to zinc reagent by transmetalation with zinc halide. But unlike the fluoroethenylzinc reagents the corresponding lithium reagents are thermally unstable. Tarrant[15] reported the potential instability of trifluoroethenyllithium, as they readily eliminate lithium fluoride leading to an alkyne, which can undergo further reactions. Also it was very well established that the stability of the trifluoroethenyllithium reagents is solvent, temperature, and concentration dependent; as ether, THF solutions are stable only at low temperature[15,16] So the Normant method of generation of the trifluoroethenylzinc reagent from the lithium reagent suffered from two major difficulties: the lithium reagent had to be generated at low temperature and the involvement of CFC type starting materials. Clearly a challenge has arisen for developing an alternative route for the synthesis of 1,2,2-trifluorostyrene by an economically viable route starting from readily available precursors. The only viable cheap, large volume, commercially available precursor for the introduction of the trifluoroethenyl group is 1,1,1,2-tetrafluoroethane (HFC-134a). Coe and co-workers[17] developed an excellent method for the generation of trifluoroethenyl and chlorodifluoroethenyllithium reagents from 1,1,1,2-tetrafluoroethylene (HFC-134a) and 1-chloro-2,2,2-trifluoroethane (HCFC-133a) at low temperature (Scheme 2). The lithium reagents thus generated were exploited for various reactions, and with metal halides as the electrophile, trifluoroethenyllithium was transformed to the trifluoroethenylmetal halide at low temperature.[18]

Recently, we have developed an alternative nonorganometallic route for the synthesis of 1,2,2-trifluorostyrenes by dehydrohalogenation of the corresponding precursors using lithium hexamethyldisilazide base.[19]

Herein we report a full account of another synthetic route that we have successfully followed for the synthesis of 1,2,2-trifluorostyrenes. This route involves the reaction of LDA with a THF solution of HFC-134a and $ZnCl_2$ at room temperature followed by Pd(0)-catalyzed cross-coupling of the transmetalated zinc reagent with aryl iodides. For a preliminary account of these results see refs 20a and 20b.

Results and Discussion

Generation of Trifluoroethenylzinc Reagent from HFC-134a and Optimization of Reaction Conditions. The generation of the trifluoroethenylzinc reagent from halocarbon HFC-134a was attempted under a variety of reaction conditions by changing the medium, base, temperature, and the zinc halide used for the transmetalation. Considering the potential thermal instability of trifluoroethenyllithium our initial experiments were performed at low temperature. Thus, reaction of HFC-134a with 2 equiv of *n*-BuLi in THF solvent at −80 °C generated the trifluoroethenyllithium. Addition of ZnI_2 to the reaction mixture generated the trifluoroethenylzinc reagent in 70% yield with a 90:10 ratio of mono ($CF_2{=}CFZnI$) and bis ($(CF_2{=}CF)_2Zn$) zinc reagents (by ^{19}F NMR analysis of the reaction mixture, vs $PhCF_3$ as internal standard). Palladium-catalyzed coupling of this zinc reagent with iodobenzene at 65 °C produced a quantitative yield of the TFS (**1**) (Scheme 3).

Although the trifluoroethenylzinc reagent and TFS were successfully generated at low temperature by the procedure outlined in Scheme 3, the low temperature utilized was not compatible with industrial production of TFS. To make this reaction feasible at ambient temperatures it was rationalized that the metalation−transmetalation process should be made in situ so that the trifluoroethenyllithium formed can be trapped before

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SCHEME 3

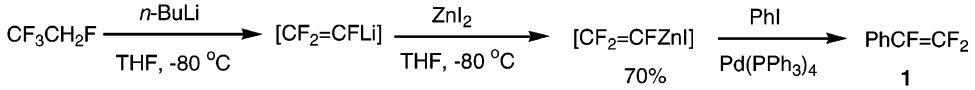
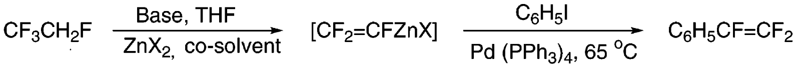


TABLE 1. In Situ Reactions of HFC-134a with Various Alkyllithium Bases in the Presence of a Zinc Salt



trial	HFC-134a, equiv	base (2 equiv)	zinc salt (1 equiv)	temp, °C	solvent/ cosolvent	% yield of zinc reagent[a]	% yield of TFS[b] (**1**)
1	1.2	*n*-BuLi	ZnI_2	−80	THF	21	
2	1.2	*n*-BuLi	ZnI_2	−26	THF	10	
3	1.2	*n*-BuLi	$ZnCl_2$	−26	THF	23	
4	1.2	*t*-BuLi	ZnI_2	−80	THF	48	
5[c]	1.2	*t*-BuLi	$ZnCl_2$	−26	THF	40	
6	4.0	*t*-BuLi	ZnI_2	−80	THF	70	
7[c]	4.0	*t*-BuLi	ZnI_2	−26	THF	66	59
8	4.0	*n*-BuLi	ZnI_2	−26	THF	21	
9[c]	4.0	*t*-BuLi	ZnI_2	−5	THF	37	
10[d]	4.0	*t*-BuLi	ZnI_2	−26	THF/HMPA	10	
11	4.0	*t*-BuLi	ZnI_2	−26	THF/DMI	57	
12	4.0	*t*-BuLi	ZnI_2	−26	THF/DMPU	63	60
13	4.0	*t*-BuLi	$ZnCl_2$·TMEDA	−26	THF	64	

[a] Yield from ZnX_2 based on ^{19}F NMR analysis of the reaction mixture (vs $PhCF_3$ as internal standard). [b] Overall yield from ZnX_2 based on ^{19}F NMR analysis. [c] Black decomposition products formed in this reaction. [d] Violent reaction with large amount of black decomposition products.

it undergoes decomposition. Table 1 summarizes the reactions of HFC-134a with various alkyllithium bases in the presence of a zinc salt. When such an in situ reaction was performed with *n*-BuLi at −80 °C the major reaction was the reaction of the *n*-BuLi with the zinc halide to produce *n*-butylzinc halide and a poor yield of the trifluoroethenylzinc reagent (Table 1, entry 1) was detected. A significantly poorer yield of the zinc reagent was observed when the reaction was performed at −26 °C, the boiling point of HFC-134a (Table 1, entry 2). When zinc chloride was used as the zinc salt a slight improvement in the yield was observed (Table 1, entry 3). It was assumed that more sterically hindered bases such as *s*-BuLi or *t*-BuLi can more effectively metalate HFC-134a in the presence of the zinc halide. So an in situ reaction was performed where the metalation reaction was carried out at −80 °C from a solution of HFC-134a and zinc iodide with *t*-BuLi as base. But unfortunately this reaction gave only a 48% yield of the zinc reagent, indicating the partial reaction of zinc halide with base (Table 1, entry 4). When the reaction was performed at −26 °C with $ZnCl_2$ a 40% yield of the zinc reagent was detected (Table 1, entry 5). In another reaction the amount of HFC-134a was increased 4-fold and the metalation with *t*-BuLi was performed at −80 °C to produce a reasonably good yield of zinc reagent (70%, Table 1, entry 6). The increase in yield of the zinc reagent was probably due to the preferential reaction of the base with the large excess of HFC-134a in the medium. When the same reaction was performed at −26 °C, a 66% yield of the zinc reagent was observed along with black decomposition products resulting from the decomposition of trifluoroethenyllithium (Table 1, entry 7).

When *n*-BuLi was substituted for *t*-BuLi in this reaction under similar reaction conditions a much lower yield of the zinc reagent was detected (Table 1, entry 8). Further increase in the temperature to −5 °C with *t*-BuLi as base produced a large amount of decomposition products with 37% yield of the zinc reagent (Table 1, entry 9). HMPA was tried as a cosolvent along with THF at −26 °C, but failed to give a clean reaction (Table 1, entry 10). Cosolvents such as 1,3-dimethyl-3,4,5,6-perhydropyrimidin-2-one (DMPU) and 1,3-dimethylimidazolidin-2-one (DMI) were reported to be excellent solvents for dehydrofluorination when used in conjunction with THF.[21] Based on this fact the metalation reaction was performed with THF−DMI and THF−DMPU mixtures to obtain 57% and 63% yield of the zinc reagent, respectively (Table 1, entries 11 and 12). Even though the reaction mixture looked much cleaner in these reactions, there was no significant improvement in the yield of the zinc reagent from the reaction where THF alone was used. We then attempted a simultaneous addition strategy where small portions of the base and electrophile were successively added to the reaction mixture to avoid the reaction of base with the electrophile. In fact such a strategy had been shown to be successful to increase the yield of the product at a relatively higher temperature, where small aliquots of the base and electrophile were added successively to the reaction vessel.[15] But unfortunately this method failed in our hands and extensive decomposition of the trifluoroethenyllithium was noted in this reaction. Alkali metal analogues of trifluoroethenyllithium like trifluoroethenylsodium or trifluoroethenylpotassium were also considered, but such species were least studied in the literature except for the patent literature and their stability seems to be questionable.[22]

Nonnucleophilic bases such as LDA, lithium-2,2,6,6-tetramethyl-4-methoxy piperidide (4-OMe-LTMP), and LHMDS were considered for effecting the metalation.

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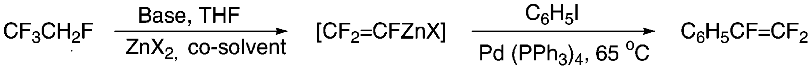
TABLE 2. In Situ Reactions of HFC-134a with Various Lithium Amide Bases in the Presence of a Zinc Salt



$$CF_3CH_2F \xrightarrow[ZnX_2,\ \text{co-solvent}]{\text{Base, THF}} [CF_2{=}CFZnX] \xrightarrow[Pd(PPh_3)_4,\ 65\ ^{\circ}C]{C_6H_5I} C_6H_5CF{=}CF_2$$

trial	HFC-134a, equiv	base (2 equiv)	zinc salt (1 equiv)	temp, °C	solvent/ cosolvent	% yield of the zinc reagent[a]	% yield of TFS[b](**1**)
1	4.0	4-OMe-LTMP	ZnI_2	−26	THF	76	
2	4.0	LHMDS	ZnI_2	−26	THF	0	
3	4.0	4-OMe-LTMP	$ZnCl_2$·TMEDA	−26	THF	82	75
4	4.0	LDA	$ZnCl_2$·TMEDA	−26	THF	86 (5)[c]	79
5	1.5	LDA	$ZnCl_2$·TMEDA	−26	THF	84 (4)[c]	71
6	1.5	LDA	$ZnCl_2$	−26	THF/TMEDA	80 (9)[c]	48[d]
7	1.5	LDA	$ZnCl_2$	−26	THF	70	
8	1.5	LDA	$ZnCl_2$	−10	THF/TMEDA	79 (9)[c]	76
9	1.3	LDA	$ZnCl_2$	0	THF/TMEDA	82 (6)[c]	81
10	1.2	LDA	$ZnCl_2$	22	THF/TMEDA	78	73
11	1.2	LDA	$ZnCl_2$	0	THF	71	60
12	1.2	LDA	$ZnCl_2$	15−20	THF	73	67
13	1.2	LDA	$ZnCl_2$	0	THF/$^iPr_2NH$	77	70
14	1.2	LDA	$ZnCl_2$	0	THF/2,2′-bipiridyl	79	70

[a] Yield from ZnX_2 based on ^{19}F NMR analysis of the reaction mixture (vs $PhCF_3$ as internal standard). [b] Overall yield from ZnX_2 based on ^{19}F NMR analysis. [c] Yields of the saturated zinc reagent ($CF_3CHFZnCl$). [d] Coupling reaction with C_6H_5Br (65 °C, 36 h).

Results of these experiments are summarized in Table 2. Reaction of HFC-134a with 4-OMe-LTMP, performed in the presence of ZnI_2 at −26 °C, produced 76% yield of the zinc reagent (Table 2, entry 1). The metalation reaction was then performed with LHMDS, but unfortunately no zinc reagent formation was detected, probably due to the poor basicity of LHMDS ($pK_a = 29.5$) compared to other lithium amide bases (Table 2, entry 2).[23] Addition of 2 equiv of *t*-BuLi to the LHMDS reaction mixture produced the zinc reagent in 63% yield and confirmed the inefficiency of LHMDS to deprotonate HFC-134a. We thought it was worthwhile to try a reaction with completely anhydrous zinc chloride as the zinc salts used herein are extremely hygroscopic even though zinc iodide was generated just before the reaction from zinc and iodine in THF. Zinc chloride forms a crystalline complex with TMEDA, which is stable to air and moisture.[24] Also it was thought that the TMEDA could act as an additive in this metalation reaction thus facilitating the zinc reagent formation.[25] A search for the zinc reagent−TMEDA complexes revealed that dialkylzinc compounds are capable of forming stable coordination complexes having well-defined stoichiometry with a variety of oxygen, nitrogen, and phosphorus and arsenic ligands.[26] A chelate structure (tetracoordinated zinc) was assumed for these 1:1 complexes with the sp^3 hybridized zinc atom. Highly unstable trifluoroisopropenylzinc reagent recently was generated in a solution of THF−TMEDA medium, where the stability of this reagent was attributed to the possible 1:1 complexation of the trifluoroisopropenylzinc reagent with TMEDA.[27] A metalation reaction performed with the $ZnCl_2$·TMEDA complex and *t*-BuLi at −26 °C produced a 64% yield of the zinc reagent (Table 1, entry 13). The zinc reagent formed was essentially mono ($CF_2{=}CFZnCl$) with traces of bis ($(CF_2{=}CF)_2Zn$) reagent appearing as shoulders in the upfield direction. We then performed this reaction using 4-OMe-LTMP. This reaction produced 82% yield of the zinc reagent (Table 2, entry 3). The success of 4-OMe-LTMP prompted us to consider a relatively inexpensive base like lithiumdiisopropylamide (LDA) for effecting this transformation. This reaction produced a clean reaction mixture (yellowish rather than the usual dark brown) with an 86% yield of the zinc reagent (Table 2, entry 4). As a next step we reduced the concentration of HFC-134a from 4 equiv to 1.5 equiv, and the reaction was performed at −26 °C with LDA as base and the $ZnCl_2$·TMEDA complex as the zinc salt. This reaction produced an 84% yield of the zinc reagent (Table 2, entry 5). Another consideration at this point was whether preformation of the complex is required or TMEDA can be added to a zinc chloride solution in THF. Thus, by using fresh solid commercial zinc chloride, a reaction was performed without preforming the complex in THF-TMEDA medium, and resulted in an excellent yield of the zinc reagent indicating preformation of complex is not required (Table 2, entry 6). Another noteworthy observation in the TMEDA-mediated reaction was the formation of traces of the saturated zinc reagent (~10%) ($CF_3CHFZnCl$) along with the trifluoroethenylzinc reagent, which gradually transformed to the trifluoroethenylzinc reagent. The presence of this species was rather surprising and is believed to be formed by the reaction of the mono anion (CF_3CHF^-) generated from HFC-134a with zinc halide before elimination of the fluoride (Scheme 4). In fact, a trace amount of such a species ($CF_3CHFSnBu_3$) was detected in the metalation reaction of HFC-134a with LDA and Bu_3SnCl.[17a]

Evidence for the formation of $CF_3CHFZnCl$ was obtained from the ^{19}F NMR and $^{19}F-^{1}H$ decoupled spectra. The ^{19}F NMR spectra showed two distinct peaks at δ −70.3 (3F, dd, $^3J_{FH} = 15.0$ Hz, $^3J_{FF} = 15.0$ Hz) and −245.1 (1F, dq, $^2J_{FH} = 48.0$, $^3J_{FF} = 16.0$ Hz). The $^{19}F-^{1}H$ decoupled spectra showed the collapse of the dd at −70.3 to a doublet ($^3J_{FF} = 15.0$ Hz) and the dq at −245.1 to a

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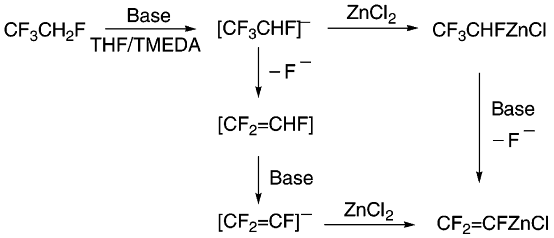
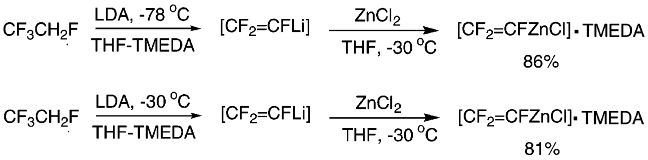
SCHEME 4



quartet ($^3J_{FF} = 15.0$ Hz). Also, the saturated zinc reagent was generated in much higher ratio (40%) when the metalation reaction was performed at lower temperatures (−80 °C) in THF−TMEDA medium. Stepwise hydrolysis of this zinc reagent mixture with a calculated amount (equivalent to the amount of trifluoroethenylzinc reagent) of concentrated HCl preferentially hydrolyzed the trifluoroethenylzinc reagent to trifluoroethylene ($CF_2{=}CFH$), which was pumped out from the reaction mixture leaving the saturated zinc reagent intact. The residual saturated zinc reagent liberated CF_3CH_2F when treated with excess concentrated HCl. The CF_3CH_2F thus generated was isolated and confirmed the presence of the saturated zinc reagent in this metalation reaction. Also quenching of the saturated zinc reagent with deuterated solvents such as D_2O, CD_3CO_2D, or DCl produced CF_3CHFD thus confirming the formation of the saturated zinc reagent. Treatment of the zinc reagent mixture with an excess of iodine at 0 °C produced only $CF_2{=}CFI$ leaving the saturated zinc reagent intact. Formation of CF_3CH_2I was not detected. But upon warming the reaction mixture to 50 °C, decomposition of the saturated zinc reagent was noted. Palladium(0)-catalyzed coupling reactions performed with zinc reagent mixtures produced a quantitative yield of the 1,2,2-trifluorostyrene (derived from trifluoroethenylzinc reagent) and again decomposition of the saturated zinc reagent was noticed under this condition. To understand the role of TMEDA in this metalation reaction, a control experiment was performed at −26 °C without the addition of a cosolvent, TMEDA, to obtain a 70% yield of the trifluoroethenylzinc reagent (Table 2, entry 7). This experiment suggested that TMEDA plays a role for obtaining a better yield of the zinc reagent by one or more of the following reasons: stabilizing the trifluoroethenyllithium at higher temperature or increasing the reactivity of zinc halide toward trifluoroethenyllithium or reducing the reactivity of the base toward the zinc halide.

SCHEME 5



The success of the transmetalation reaction in TMEDA−THF at −26 °C prompted us to try this reaction at higher temperatures. The reaction performed at −10 and 0 °C gave good yield (>80%) of the trifluoroethenylzinc reagent (Table 2, entries 8 and 9). When the reaction was performed at room temperature (22 °C), 78% yield of the trifluoroethenylzinc reagent with a clean reaction mixture (Table 2, entry 10) was produced. Reactions without TMEDA at 0 and 20 °C also produced reasonably good yields of the zinc reagent (Table 2, entries 11 and 12), which could be due to the presence of diisopropylamine liberated in the medium acting as an amine cosolvent instead of TMEDA. We then tried other ligands similar to TMEDA which can complex with $ZnCl_2$: 2,2′-bipyridyl, diisopropylamine, and triethylamine. Reactions performed with an excess of diisopropylamine as cosolvent at −26 °C and higher temperatures (0 and 20 °C) also produced a reasonably good yield of the trifluoroethenylzinc reagent (>75%) (Table 2, entry 13). Reactions performed with 2,2′-bipyridyl at different temperatures (−80, −26, 0, 20 °C) produced a good yield of the trifluoroethenylzinc reagent (Table 2, entry 14). Yields of the zinc reagent dropped from 92% to 72% when the temperatures were increased from −80 to 20 °C. There was not much loss in yield of the zinc reagent when the reaction was performed at 0 or 20 °C. Change of cosolvent to triethylamine did not significantly improve the yield of the trifluoroethenylzinc reagent.

Stability of [$CF_2{=}CFLi$] and Nature of the Trifluoroethenylzinc Reagent. We next investigated the stability of the trifluoroethenyllithium in TMEDA−THF medium and also the nature of the zinc reagent formed in this metalation reaction. The excellent formation of the zinc reagent at temperatures close to room temperature made us believe that the intermediate trifluoroethenyllithium species is stable in the TMEDA medium. To test this hypothesis we have generated trifluoroethenyllithium by the metalation of HFC-134a using LDA at −78 °C in THF−TMEDA medium and the clear solution obtained was slowly warmed to room temperature. The color of the solution slowly turned slightly brown when the temperature of the reaction mixture reached −25 °C and black solid decomposition products formed at −20 to −15 °C, and addition of a solution of $ZnCl_2$ in THF to this medium produced only 5% of the zinc reagent with traces of reduced product. In another reaction the clear solution of trifluoroethenyllithium generated in THF−TMEDA at −78 °C was warmed to −30 °C (no significant color change noticed) and slowly transmetalated with a solution of $ZnCl_2$ in THF. ^{19}F NMR analysis of this mixture showed an 86% yield of the trifluoroethenylzinc reagent (Scheme 5). This experiment demonstrated that the trifluoroethenyllithium generated is stable even at −30 °C in the THF−TMEDA medium. The success of this experiment prompted us to generate the trifluoroethenyllithium at −30 °C and then transmetalate it with zinc chloride at that temperature in the THF−TMEDA medium. This experiment when performed produced a clear solution of the trifluoroethenyllithium and the trifluoroethenylzinc reagent in 81% yield (Scheme 5). A similar reaction performed without TMEDA showed much less stability for the trifluoroethenyllithium as the decomposition was noticed at −45 °C with formation of a black reaction mixture even in the presence of diisopropylamine in the medium. But the thermal stability expressed by trifluoroethenyllithium in this reaction (THF/$^iPr_2NH$) was better than that generated in THF medium by metalation with use of alkyllithium bases (THF solutions of trifluoroethenyllithium are known to decompose at temperatures higher than −78 °C).[16] We have cross checked the thermal stability of trifluoroethenyllithium in THF by performing the metalation of HFC-134a with *n*-BuLi at −80 °C in THF medium and

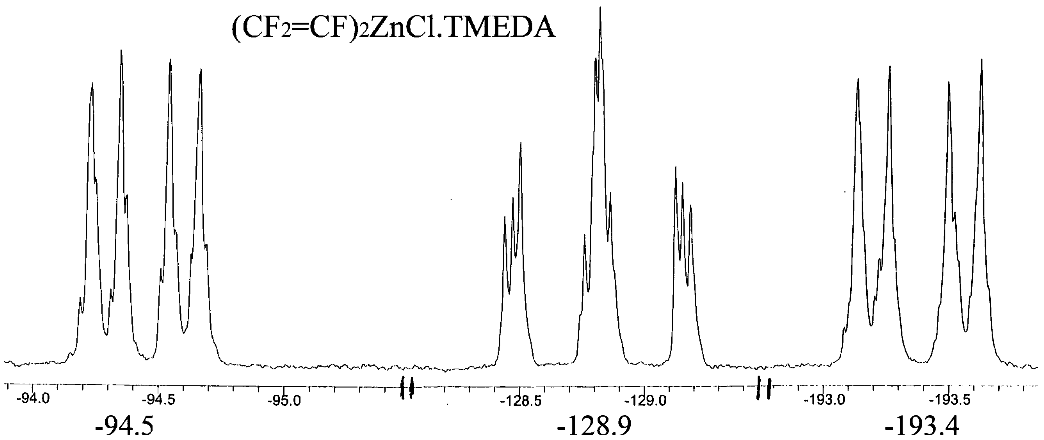


FIGURE 1. ^{19}F NMR spectrum of the bis-trifluoroethenylzinc reagent in THF−TMEDA medium.

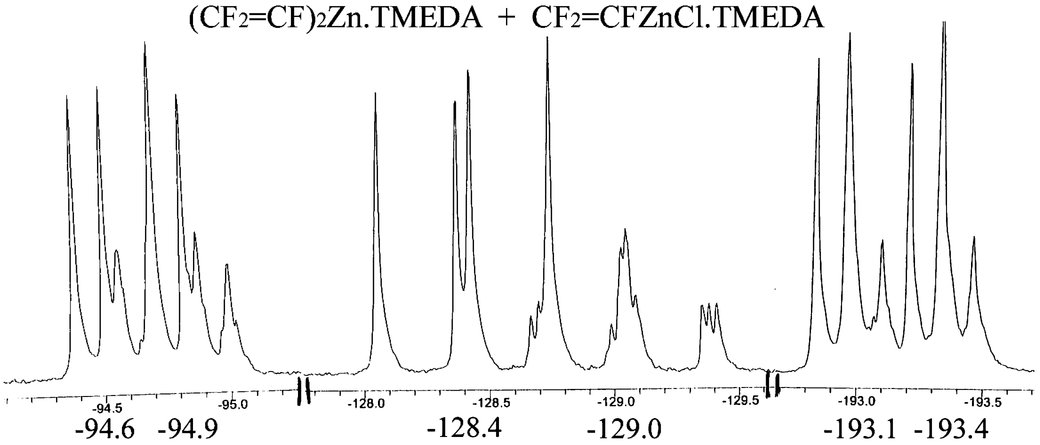


FIGURE 2. ^{19}F NMR spectrum of the mono- and bis-trifluoroethenylzinc reagents in THF−TMEDA (mono/bis = 75:25) medium.

warming the resulting trifluoroethenyllithium solution to higher temperatures. At −70 °C the clear solution turned to black and at −50 °C complete decomposition was the result with no trifluoroethenylzinc reagent formation upon transmetalation with zinc chloride. In another experiment the trifluoroethenyllithium generated at −80 °C was warmed to −60 °C and when the dark reaction mixture was quenched at −60 to −55 °C produced 78% yield of the zinc reagent, which shows there is trifluoroethenyllithium present even at −55 °C. On the basis of these experiments we have concluded that amines in the medium enhance stability for the trifluoroethenyllithium, especially TMEDA, and the decomposition temperature of trifluoroethenyllithium in TMEDA−THF solution lies somewhere around −25 °C.

We have also performed experiments to test the nature of the zinc reagents formed in this metalation reaction. During our experiments (Table 2) it was noticed that the zinc reagent was obtained as a mixture of mono and bis species in varying ratio from 60:40 to 85:15. The ^{19}F chemical shifts of the mono and bis zinc reagent varied slightly depending on the cosolvent (THF or THF/TMEDA or THF/diisopropylamine, THF/2,2′-bipyridyl) and the counterion (Cl, Br, I). The zinc reagent generated in THF/diisopropylamine medium showed spectral patterns corresponding to both mono and bis zinc reagents complexed to THF and diisopropylamine with a slight difference in the chemical shift in the upfield direction. Addition of TMEDA to the medium produced one set of peaks resulting from the preferential complexation of the mono and bis zinc reagent to TMEDA over diisopropylamine or THF. An interesting complex splitting pattern was noticed for the ^{19}F NMR spectra of the bis zinc reagent generated in the TMEDA medium. The complex splitting pattern observed for the bis reagent in TMEDA medium was absent in the case of both the mono and bis zinc reagents generated in THF/$^{i}Pr_2NH$ medium and for the mono zinc reagent in TMEDA. To unequivocally confirm the mono and bis zinc reagent assignments, we have performed a series of experiments (Scheme 6). At first we attempted to generate only the bis zinc reagent by using 0.5 equiv of zinc chloride rather than the usual 1 equiv. To our joy this experiment exclusively produced only the bis zinc reagent (Figure 1) whose chemical shifts and splitting pattern matched exactly for the minor component of the usual reaction, thus demonstrating that the major zinc reagent in the usual reaction is the mono reagent. We have added a slight excess of $ZnCl_2$ (1.0 equiv) to this reaction mixture to shift the equilibrium (Scheme 6) to the mono side and obtained a 75:25 mixture of mono and bis zinc reagents (Figure 2) proving that our assignments of mono and bis zinc reagents are correct. In another experiment we have increased the concentration of $ZnCl_2$ from 0.5 to 0.75 equiv and this reaction produced a 40:60 mixture of mono and bis zinc reagent and the ratio changed to 75:25 when excess $ZnCl_2$ was

F^a = -94.5 (ddm), F^b = -128.9 (ddm),

F^c = -193.4(ddm):

${}^3J_F^{ac} = {}^3J_F^{ca}$ = 33.0 Hz, ${}^2J_F^{ab} = {}^2J_F^{ba}$ = 90.0 Hz,

${}^3J_F^{bc} = {}^3J_F^{cb}$ = 104.0 Hz

$F^{a'}$ = -94.6 (dd), $F^{b'}$ = -128.4 (dd),

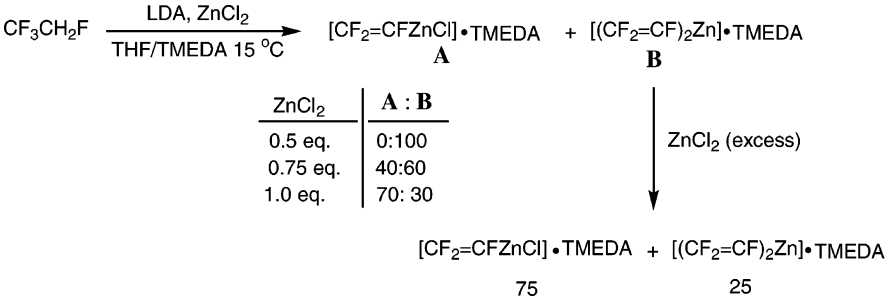
$F^{c'}$ = -193.1(dd):

${}^3J_F^{a'c'} = {}^3J_F^{c'a'}$ = 34.0 Hz, ${}^2J_F^{a'b'} = {}^2J_F^{b'a'}$ = 90.0 Hz,

${}^3J_F^{b'c'} = {}^3J_F^{c'b'}$ = 105.0 Hz

FIGURE 3. Mono- and bis-trifluoroethenylzinc reagents complexed to TMEDA and their ^{19}F NMR chemical shifts.

SCHEME 6



SCHEME 7

$$2\ [CF_2{=}CFZnCl]\bullet TMEDA \rightleftharpoons [(CF_2{=}CF)_2Zn]\bullet TMEDA + ZnCl_2$$

SCHEME 8

$$CF_3CH_2F + Bu_3SnCl \xrightarrow[\text{THF, 15-20 °C}]{\text{LDA}} CF_2{=}CFSnBu_3$$

64%

added to this reaction mixture. It was not possible to generate exclusively the mono zinc reagent even with a large excess of $ZnCl_2$ (3.0 equiv). The Schlenk equilibrium for the TMEDA complexes of mono and bis zinc reagents is shown in Scheme 7.

The ^{19}F NMR chemical shifts for the TMEDA complexes of mono and bis trifluoroethenylzinc reagents are represented in Figure 3.

We have also applied the metalation strategy for the synthesis of the trifluoroethenyltin reagent ($CF_2{=}CFSnBu_3$). Metalation of HFC-134a in the presence of Bu_3SnCl produced the trifluroethenyltin reagent in a 69% NMR yield. From this reaction mixture trifluoroethenyltin was isolated in 64% yield by column chromatography (Scheme 8).

Coupling Reaction of Trifluoroethenylzinc Reagent with Aryl iodides. After standardizing the conditions of the metalation reaction at 15−20 °C in the THF−TMEDA medium, we have attempted the palladium-catalyzed cross-coupling reaction of the zinc reagent with aryl iodides. In fact during our optimization experiments in most cases the coupling reactions were performed with $Pd(PPh_3)_4$ and aryl iodide resulted in a quantitative yield of the TFS (**1**) (Tables 1 and 2). To standardize conditions for the coupling reaction, 1-fluoro-4-iodobenzene was chosen, since it can be easily monitored through ^{19}F NMR analysis of the reaction mixture. Reactions were performed with a 1:1 and 1:0.9 zinc reagent:iodide ratio produced a reaction mixture with traces of unreacted iodide. Since the unreacted iodide cannot be easily removed from the product (both have the same R_F and close boiling points) we elected to perform the coupling reaction with iodide as the limiting reagent. When the reaction was performed with a 1:0.8 ratio of zinc reagent and aryl iodide in THF−TMEDA medium, the corresponding 4-fluoro-substituted styrene **2** (87% by ^{19}F NMR) was produced along with a small amount of an addition−elimination product (0.5:1 cis/trans, p-$FC_6H_4CF{=}CFOBu$). But the coupling reaction in the absence of TMEDA (from the zinc reagent generated in THF medium) produced exclusively (99% by ^{19}F NMR) the styrene **2** with no addition−elimination product formation (Table 3). Isolation of the product by column chromatography produced 64% yield of pure **2**.[28] Even though the presence of TMEDA was important for obtaining a better yield of the trifluoroethenylzinc reagent, formation of side products during the Pd(0)-catalyzed coupling process and the additional cost of another reagent and its removal from the reaction mixture were disadvantageous.

Finally the best conditions for the generation of the trifluoroethenylzinc reagent and for the coupling reaction were chosen as follows: addition of LDA (50.0 mmol, ~1.0 M) to a medium of zinc chloride (25.0 mmol) and HFC-134a (30.0 mmol) in THF (15.0 mL) and heating of the concentrated solution of zinc reagent in THF with the aryl iodide (1:0.8 ratio) with 1.5 mol % of $Pd(PPh_3)_4$. When iodobenzene was used for the coupling reaction with the trifluoroethenylzinc reagent, a 95% yield (^{19}F NMR) of TFS (**1**) was produced. Isolation of the product by column chromatography resulted in a 69% yield of pure **1**.[6]

We then carried out this synthesis for a series of aryl iodides with various substituents in the aromatic ring (Table 3). Generally the reaction was complete when

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TABLE 3. Synthesis of 1,2,2-Trifluorostyrenes

$$CF_3CH_2F \xrightarrow[\text{THF, 15-20 °C}]{\text{LDA, ZnCl}_2} [CF_2{=}CFZnCl] \xrightarrow[\text{rt or 65 °C, THF}]{\text{ArI, Pd(PPh}_3)_4\text{, (1.5 mol\%)}} ArCF{=}CF_2$$

Ar	product (**1**−**18**)	temp, °C; time, h	NMR yield	isolated yield,[a] %
C_6H_5−	**1**	65; 3	99	69
p-FC_6H_4−	**2**	65; 4	95	64
m-FC_6H_4−	**3**	65; 2	99	63
o-FC_6H_4−	**4**	65; 2	98	74
p-$NO_2C_6H_4$−	**5**[b]	60; 1	50	37
m-$NO_2C_6H_4$−	**6**	rt; 15	84	61
p-$CF_3C_6H_4$−	**7**	65; 1.5	86	66
m-$CF_3C_6H_4$−	**8**	65; 1	95	67
o-$CF_3C_6H_4$−	**9**	65; 48	93	61
p-$OMeC_6H_4$−	**10**	60; 1	94	82
m-$OMeC_6H_4$−	**11**	65; 1	99	85
o-$(CH_3)_2CHC_6H_4$−	**12**	65; 2	96	86
m-ClC_6H_4−	**13**	60; 2	97	78
p-ClC_6H_4−	**14**	60; 2	96	82
p-BrC_6H_4−	**15**[c]	rt; 18	95	75
p-IC_6H_4−	**16**	rt; 12	90	71
1-naphthyl	**17**	60; 2	98	83
2-thienyl	**18**[d]	60; 1	84	59

[a] Yield of styrene after column chromatography of the reaction mixture; all products gave satisfactory ^{19}F, ^{1}H, ^{13}C NMR (>95% purity) and GC-MS data. [b] A mixture of unidentified products formed in this reaction. [c] No bis-styrene was detected after 12 h at room temperature; ~3% of bis-styrene was formed after 24 h at room temperature. [d] A better NMR yield (95%) was noticed with stirring at rt for 24 h.

heated at 65 °C for 1−3 h for most of the substrates. Most of these coupling reactions were also feasible even at room temperature with stirring for a prolonged time. Iodides with electron withdrawing groups in the benzene ring coupled smoothly at 65 °C in 2−4 h to produce the corresponding styrenes in reasonably good yield. From 1-fluoro-3-iodobenzene the corresponding styrene **3** was isolated in 63% yield.[29] 1-Fluoro-2-iodobenzene was also converted to the corresponding styrene **4** in 74% yield.[30] The coupling reaction with 1-iodo-4-nitrobenzene produced a complex red reaction mixture from which the corresponding styrene **5** was isolated in 37% yield.[11a] The coupling reaction with 1-iodo-3-nitrobenzene performed at room temperature for 15 h produced the corresponding styrene **6** in 61% isolated yield.[13b]

4-Iodobenzotrifluoride was transformed to the corresponding styrene **7** in 66% yield when heated with trifluoroethenylzinc reagent and $Pd(PPh_3)_4$ at 65 °C for 1 h.[31] Similarly from 3-iodobenzotrifluoride, the product styrene **8** was isolated in 67% yield.[13a] Reaction of 2-iodobenzotrifluoride with trifluoroethenylzinc reagent was sluggish under the usual reaction conditions and the complete conversion was observed when the reaction mixture was heated at 65 °C for 48 h with a slight excess of the palladium catalyst (2.0 mol %). Column chromatographic isolation produced the corresponding styrene **9** in 61% yield.[13b] Iodides with electron donating groups reacted very smoothly under the coupling reaction conditions to produce the corresponding styrenes in excellent yield. 3- and 4-iodoanisoles reacted with the trifluoroethenylzinc reagent at 60 °C for 1 h to produce the corresponding styrenes **10** and **11** in 85% and 82% isolated yields, respectively.[13b,29] Reaction with 2-iodoisopropylbenzene was performed to test the effect of the bulky isopropyl group at the ortho position for this cross-coupling reaction. This reaction proceeded smoothly under normal coupling reaction conditions to produce the corresponding styrene **12** in 86% yield.[13b] We then compared the reactivity of other aryl halides such as bromides and chlorides in this coupling reaction. Thus, a reaction of 1-chloro-3-iodobenzene was treated with trifluoroethenylzinc reagent and palladium under normal coupling reaction conditions and complete conversion of the iodide to styrene **13** was noted keeping the ring chlorine intact. The isolated yield of **13** was 78%.[32] 1-Chloro-4-iodobenzene was also tried and resulted in the corresponding styrene **14** in 82% yield under similar conditions.[13b] The coupling reaction of bromobenzene with the trifluoroethenylzinc reagent was also attempted, where the bromobenzene was heated with the zinc reagent at 65 °C for 36 h to produce a 48% overall yield (^{19}F NMR) of **1** (Table 2, entry 6). Reaction of 1-bromo-4-iodobenzene with the trifluoroethenylzinc reagent produced the corresponding bromo-substituted mono styrene **15** along with traces of the bis styrene **16** (mono/bis 1:0.03) when treated with palladium catalyst at room temperature for 18 h.[20a] The isolated yield of the product was 75%. The bis styrene **16** was produced exclusively from 1,4-diiodobenzene by treating it with the zinc reagent and palladium catalyst at room temperature for 12 h.[13b] The isolated yield of **16** was 71%. 1-Iodonaphthalene coupled with the trifluoroethenylzinc reagent under normal coupling reaction conditions to produce the corresponding styrene **17** in 83% isolated yield.[33] The heterocyclic iodide, 2-iodothiophene, reacted with the trifluoroethenylzinc reagent within 1 h under normal coupling reaction conditions to produce a mixture of products from which the product styrene **18** was isolated in 59% yield.[13a]

Conclusions

In summary, a novel strategy was developed for the formation of the trifluoroethenylzinc reagent from the readily available, economically viable, halocarbon HFC-134a. Operating this methodology at 0 °C or at room temperature was a challenge due to the potential instability of the trifluoroethenyllithium. By systematic standardization of the metalation experiments by manipulating solvent, cosolvent, temperature, zinc salt, and the base, trifluoroethenylzinc reagent generation was achieved in good yields near room temperature. The palladium-catalyzed coupling reaction of the trifluoroethenylzinc reagent with aryl iodides was carried out under mild conditions to produce TFS and substituted trifluorostyrenes in essentially quantitative yields. Trifluoroethenyllithium showed exceptional thermal stability in THF−TMEDA medium. Experimental evidence for the mono anion of HFC-134a was obtained by the trapping

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(33) Kazennnikova, G. V.; Talalaeva, T. V.; Zimin, A. V.; Simonov, A. P.; Kocheshkov, K. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1961**, 835−838 (Engl. Transl. pp 772−774).

of the mono anion with zinc halide in TMEDA medium. The mono and bis nature of the zinc reagent was unequivocally demonstrated by complexation experiments with TMEDA. The in situ metalation strategy was successfully applied for the synthesis of the trifluoroethenyltin reagent ($CF_2{=}CFSnBu_3$) by performing the metalation in the presence of Bu_3SnCl.

Experimental Section

General Procedure for the Preparation of the Trifluoroethenylzinc Reagent from HFC-134a. A 250-mL three-necked flask fitted with a dry ice/2-propanol condenser, septum, and low-temperature thermometer was charged with anhydrous $ZnCl_2$ (3.42 g, 25.0 mmol) and THF (15.0 mL) under a N_2 atmosphere. The suspension was cooled to 15 °C and HFC-134a (2.5 mL, 30.0 mmol) was condensed into the slurry. Then an LDA solution [generated from diisopropylamine (7 mL, 50.0 mmol) and *n*-BuLi (20.0 mL, 2.5 M, 50.0 mmol) in THF (25.0 mL) at 0 °C] solution was slowly added (35 min) through a cannula to the HFC-134a/$ZnCl_2$ slurry while keeping the temperature at 15−20 °C (the tip of the cannula was dipped into the THF to avoid decomposition of the trifluoroethenyllithium, formed by the reaction of gaseous HFC-134a with LDA, at the tip). The pale yellow reaction mixture was stirred for 1 h and allowed to warm to room temperature. The ^{19}F NMR analysis of the zinc reagent indicated a 73% (18.3 mmol) yield.

General Procedure for the Preparation of 1,2,2-Trifluorostyrenes. $C_6H_5CF{=}CF_2$ (1): The zinc reagent was concentrated to about half its volume (40.0 mL; 17.5 mmol) then 2.85 g (14.0 mmol) of iodobenzene and 0.28 g (1.5 mol %) of $Pd(PPh_3)_4$ were added to the solution of the zinc reagent. The reaction mixture was heated at 65 °C for 3 h, and complete conversion of the zinc reagent to TFS was detected (99% by ^{19}F NMR analysis). The mixture was cooled and triturated several times with pentane, and the solvent removed by careful rotoevaporation (the distillate collected in the receiver showed traces of TFS). Silica gel column chromatography (elution with pentane) gave 1.52 g (9.6 mmol, 69%) of pure $C_6H_5CF{=}CF_2$ as a colorless liquid. The spectroscopic data were in agreement with a sample prepared previously in this laboratory.[13b]

Acknowledgment. The authors greatly acknowledge Dr. Charles Stone for insight into this project and thank Ballard Power Systems Inc. BC, Canada and NSF for financial support.

Supporting Information Available: Experimental and characterization data for all the 1,2,2-trifluorostyrenes (**1**−**18**) prepared by this methodology. This material is available free of charge via the Internet at http://pubs.acs.org.

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