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Synthesis of Fluorinated Dienes by Palladium-Catalyzed Coupling Reactions

Floris A. Akkerman, Rainer Kickbusch, and Dieter Lentz*[a]

Abstract: The synthesis of partly fluorinated 1,3- and 1,4-dienes by palladium-catalyzed coupling makes these compounds available on the laboratory scale. Several catalyst systems were tested to maximize the yields and minimize the by-products. The molecular structures of 1,1,2,4,4-pentafluorobutadiene, chloro(*N*,*N*′-tetramethylethylenediamine)(trifluorovinyl)zinc, PCy_2R, and $P(O)Cy_2R$ (Cy = cyclohexyl, R = 2-(1-naphthyl)phenyl) were elucidated by X-ray crystallography.

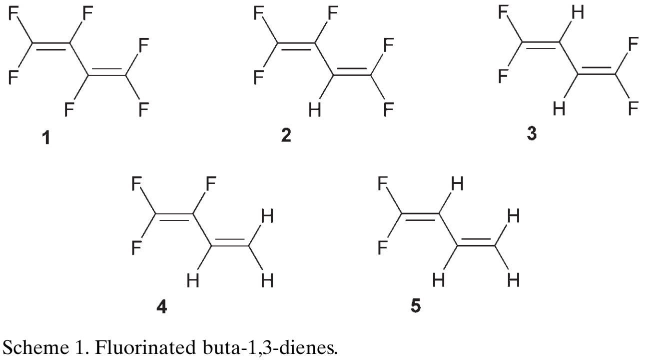
Keywords: C–C coupling · crystal structure · dienes · fluorine · palladium

Introduction

Since the early works of Negishi,[1] Miyaura and Suzuki,[2] and Stille,[3] Palladium-catalyzed C–C-coupling reactions have evolved into one of the most important tools in organic synthesis.[4] The majority of these reactions concern aryl–aryl or aryl–vinyl couplings. The coupling of vinyl stannanes with vinyl halides to yield 1,3-dienes, originally studied by the Stille group,[5] is much less developed but has been widely used in the total synthesis of natural products.[6] Studies of the synthesis of 1,4-dienes are even less common.[7] Several palladium-catalyzed reactions of fluorinated alkenyl building blocks with aromatic and vinyl compounds to yield fluorine-substituted styrenes and 1,3-dienes have been studied by the groups of Burton,[8] Normant,[9] McCarthy,[10] Percy,[11] and DesMarteau.[12] The chemistry of fluorinated allyl and vinyl organometallic compounds, among other systems, has been reviewed by Burton et al., including their application in coupling reactions.[13] There are only a few publications about Pd-catalyzed allyl–vinyl cross-coupling reactions with fluorinated components.[13,14,15] However, there exists a very efficient synthesis of 1,1,2-trifluoropenta-1,4-diene (**6**) from trifluoroethenyl zinc bromide and allyl bromide by copper-catalyzed coupling, which was reported by Gard, Burton, and co-workers.[16] Iron- and copper-mediated reactions have been used to prepare symmetric and unsymmetric 1,3-dienes from fluorinated vinyl zinc halides,[17] vinyl stannanes,[18] and vinyl halides.[13,19] There have also been direct coupling reactions with copper[20] reagents.

Recently, we used the Negishi coupling to prepare 1,1,4,4-tetrafluorobutadiene, the key precursor in the synthesis of 1,1,4,4-tetrafluorobutatriene.[21] Since then, other groups have extended the variety of fluorinated compounds prepared by vinyl–vinyl coupling reactions.[22–26] A particularly elegant method of synthesizing symmetrical dienes by Pd-catalyzed coupling of vinyl halides by generation of vinyl stannanes in situ with $(Bu_3Sn)_2$ was published recently by Xu and Burton.[22c] As a continuation of our work, we report herein the synthesis of a number of fluorine-substituted 1,3- and 1,4-dienes (Schemes 1 and 2).

Butadienes **1**–**5** have been known since the 1950s,[27] but so far there exists no convenient laboratory-scale synthesis for dienes **2**–**5**. Hexafluorobutadiene **1** was prepared by cou-



Scheme 1. Fluorinated buta-1,3-dienes.

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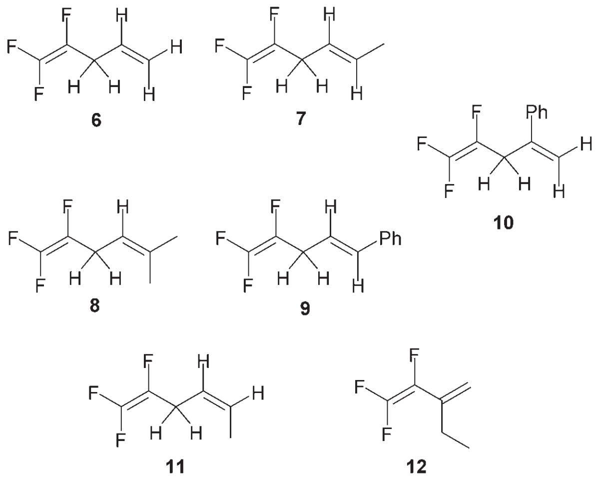


Scheme 2. 1,1,2-Trifluoro-1,4-dienes **6**–**11** and 1,1,2-trifluoro-3-ethylbutadiene (**12**).

pling of trifluoroiodoethene[19] with stoichiometric amounts of activated copper and by oxidative coupling of trifluoroethenyl zinc bromide with copper(II) bromide.[13] Trifluoroiodoethene can be prepared from commercially available trifluorobromoethene[22a] or, alternatively, from trifluoroethenyl lithium.[9b] For application in polymerization experiments, chemical industry has developed a variety of methods as described in the patent literature, most of which involve high pressures, high temperatures, or expensive equipment.[28] Of the fluorinated dienes, only hexafluorobutadiene has found technical application, as a monomer and in plasma etching. Consequently, the industrial synthesis is still being improved.[29]

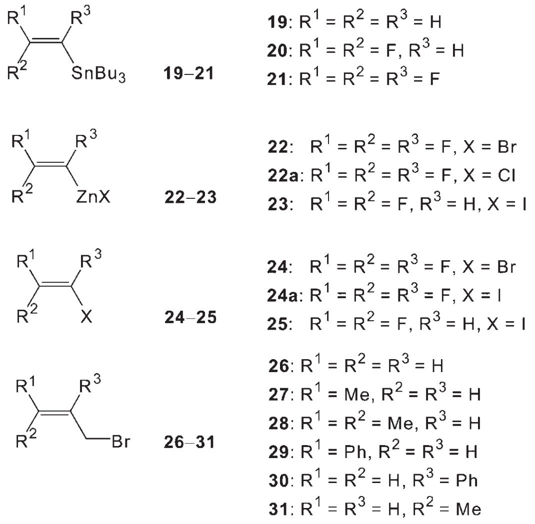
The 1,4-dienes **6**–**11** presented in Scheme 2 can be prepared by using either Negishi or Stille reactions for coupling of an organometallic trifluorovinyl species (**21**, **22**) with an allylic bromide (**26**–**31**). The allyl compounds were selected mainly for their availability. The 1,3-diene **12** was obtained as a by-product with **7** and **11**.

Abstract in German: Teilfluorierte 1,3- und 1,4-Diene sind nun im Labormaßstab durch Palladium katalysierte C–C Kupplungsreaktionen leicht zugänglich. Es wurden unterschiedliche Katalysatorsysteme zur Optimierung der Ausbeute und der Reinheit der Produkte untersucht. Die Strukturen von 1,1,2,4,4-Pentafluorbutadien, Chloro(*N*,*N*′-tetramethylethylendiamin)(trifluorvinyl)zink, PCy_2R, und $P(O)Cy_2R$ (Cy = Cyclohexyl, R = 2-(1-Naphthyl)phenyl) konnten durch Röntgenbeugung an Einkristallen aufgeklärt werden.

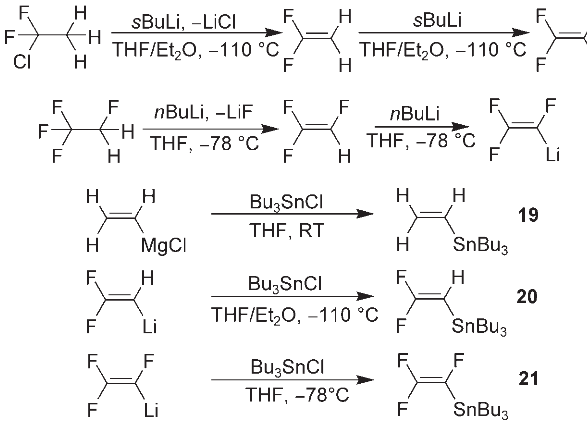
Results and Discussion

To synthesize butadienes **1**–**5** and 1,4-dienes **6**–**11**, we used a variety of C_2 building blocks (Scheme 3). Fluorinated ethenes can be obtained from some specialized suppliers, but most of them are expensive and are not easy to transport owing to instability or customs regulations. Therefore, we focused on four starting materials for our syntheses: 1,1-difluoroethene and trifluorobromoethene, which are used in polymer synthesis, and 1,1,1,2-tetrafluoroethane and 1-chloro-1,1-difluoroethane, which are refrigerants widely used in air conditioners. These can easily be converted into the desired reagents by the reactions outlined in Scheme 4.

ICl was added to 1,1-difluoroethene to form 1-iodo-2-chloro-2,2-difluoroethane,[27a] which was converted into 1-iodo-2,2-difluoroethene in high yields with potassium *tert*-butanolate. To avoid by-product formation resulting from nucleophilic attack at the CF_2 group, the *tert*-butanolate has



Scheme 3. Vinyl and allyl building blocks.



Scheme 4. Synthesis of tributylethenyl stannanes.

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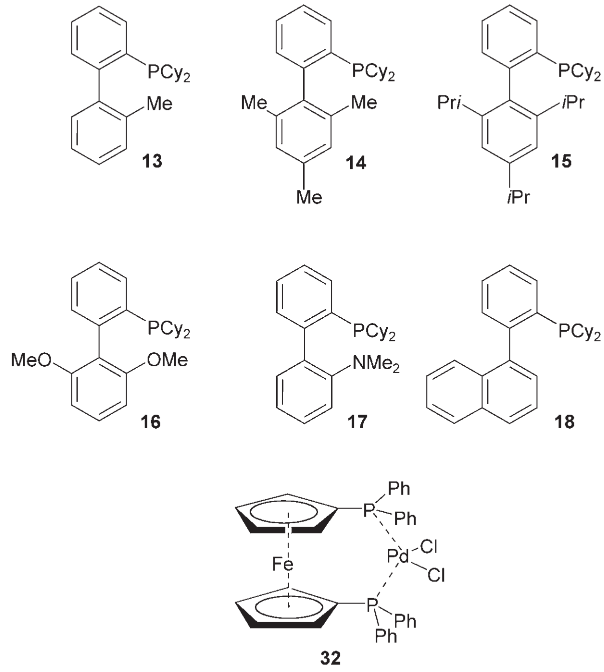
to be added to the ethane. Lithiation of 1,1-difluoroethene at −110 °C following a procedure described by Sauvetre and Normant[30] gave 2,2-difluoroethenyl lithium. The same compound was formed from 1-chloro-1,1-difluoroethane and 2 equivalents of *sec*-butyllithium. The unstable difluoroethenyl lithium reagent was trapped with tributylchlorostannane to form **20** as a colorless air-stable liquid. This stannane was prepared by Burton and co-workers via (2,2-difluoroethenyl)triethylsilane.[31] Tributyltrifluoroethenylstannane **21** was formed similarly in excellent yield by the reaction of tributylchlorostannane with trifluoroethenyl lithium, which was obtained from 1,1,1,2-tetrafluoroethane and 2 equivalents of *n*-butyllithium at −78 °C[32] or with lithium diisopropylamide (LDA) at room temperature.[33] Compound **21** can also be prepared with trifluorovinyl Grignard[34,35] or zinc reagents.[36] Both stannanes were easily purified by vacuum distillation. Reaction of 1-iodo-2,2-difluoroethene and 1-bromo-1,2,2-trifluoroethene with zinc in *N*,*N*-dimethylformamide (DMF) generated the zinc reagents **22** and **23**, respectively.[37,38] An alternative procedure for the synthesis of **23** with 1,1,1,2-tetrafluoroethane, LDA, and zinc chloride or bromide[39] cannot be used in our case owing to problems in separating the solvent THF from the butadienes. However, this zinc reagent as well as the one formed from the reaction of 1,1,1,2-tetrafluoroethane with *n*-butyl lithium can be used in THF if less volatile products were synthesized.

Stille Coupling: Catalyst Optimization

As palladium compounds are expensive materials, we tried to improve the efficiency of our syntheses in two ways: we moved from a premade Pd^0 complex to a catalyst system generated in situ from a simple palladium(II) salt and a phosphine ligand, thus reducing the molecular weight of the palladium compound used, and we decreased the amount of catalyst used altogether from 1–3 mol % to as low as 0.25 mol %.

By leaving behind the “standard” catalyst used so far (tetrakis(triphenylphosphanyl)palladium), another problem was almost eliminated: the air sensitivity of the catalyst compound.[8] Palladium acetate and the phosphines we used are air-stable and thus easy to handle, and as long as the coupling reaction itself takes place under anaerobic conditions, the activity of the catalyst is preserved much longer than in open systems.

According to Buchwald and co-workers,[40] dicyclohexyl-(2-biaryl)phosphines **13**–**18** with various substituents on the biaryl moiety (Scheme 5) are excellent cocatalysts in Suzuki coupling reactions. We compared six of these catalyst systems and another promising Pd complex, dichloro-[1,1′-bis-(diphenylphosphanyl)ferrocene]palladium(II) (**32**),[41] with the “standard” catalyst used so far, tetrakis(triphenylphosphanyl)palladium(0). In contrast to the studies of Buchwald and co-workers, we tried to optimize Stille coupling rather than Suzuki coupling, because the boronic acid derivatives required for our syntheses are not readily available.



Scheme 5. Buchwald phosphines **13**–**18** and $[Pd(dppf)Cl_2]$ (**32**) (Cy = cyclohexyl).

Optimization experiments were carried out in sealed 8-mm glass tubes, which were placed in 10-mm NMR tubes for ^{19}F NMR spectroscopy. The tubes were heated in an oven to the desired temperature. Conversion was considered to be complete when the ^{19}F NMR signals of one of the initial compounds had disappeared. Product purity was roughly determined by comparison of the peak heights of the product with those of the by-products, so this value can only include fluorine-containing compounds. A catalyst system was considered best when the reaction proceeded to total conversion in a short time and resulted in a highly pure product.

The conditions for these best results are summarized in Table 1. Details are given in the Supporting Information.

Vinyl–Vinyl Couplings

As shown in Table 1, hexafluorobutadiene was formed in high purity by the reaction of **21** and **24** with the phosphine **13** catalyzed by $[Pd_2(dba)_3]$. The synthesis of **2** proceeded well by the reaction of **20** with **24**. In the reaction of **21** with **25**, the purity was always low. These results are remarkable, as iodide **25** is expected to be more reactive in cross-coupling reactions than bromide **24**. Homocoupling (to yield **1**) is an important side reaction, which can even dominate over the desired cross-coupling. Butadienes **1** and **2** could not be separated by simple distillation. The difluorovinyl compound **20** did not give a homocoupled product under the conditions reported in Table 1.

The synthesis of **3** seems to be rather indifferent towards the choice of phosphine ligands. The only exception is a

Table 1. Summary of small-scale catalyst optimization.

Component 1	Component 2	Desired product	Catalyst system ([mol %])	t/T	Conversion [%] (purity [%])
21	**24**	**1**	$[Pd_2(dba)_3]$/**13** (0.25/1.25)	17 h/60 °C	100 (95)
20	**24**	**2**	$Pd(OAc)_2$/**15** (0.25/1.25)	24 h/60 °C	100 (96)
21	**25**	**2**	$Pd(OAc)_2$/**17** (0.25/1.25)	24 h/60 °C	100 (50)
20	**25**	**3**	$Pd(OAc)_2$/**14** (0.25/1.25)	6 h/60 °C	100 (97)
19	**24**	**4**	$Pd(OAc)_2$/**17** (0.25/1.25)	72 h/60 °C	75 (80)
19	**25**	**5**	**32** (0.25)	6 days/25 °C	100 (99)
21	**26**	**6**	$[Pd_2(dba)_3]$/**13** (0.25/1.25)	10 days/25 °C	100 (78)
21	**29**	**9**	$[Pd_2(dba)_3]$/**13** (0.25/1.25)	6 days/25 °C	100 (59)
21	**30**	**10**	$[Pd(PPh_3)_4]$ (0.5)	4 days/25 °C+1 day/75 °C	100 (56)

dba = dibenzylideneacetone.

slow reaction when the combination of $Pd(OAc)_2$ with the weaker donor PPh_3 was employed as catalyst. The combined effects of iodide **25** rather than a bromide as well as the more reactive stannane **20** make this reaction generally faster than those described above. As the homocoupling also yielded **3**, this was not a significant problem in this case.

The synthesis of **4** from **19** and **24** did not proceed satisfactorily, as none of the small-scale experiments could be brought to completion within 3 days, and several samples showed no reaction at all. Strangely, with catalyst **32**, the product vanished after heating for more than 8 h. However, catalyst **32** is the best choice for the synthesis of **5**. This reaction was complete after 6 days at room temperature, whereas the samples had to be heated with all the other catalyst systems.

Allyl–Vinyl Couplings

Allyl–vinyl Stille couplings are known to proceed more easily than vinyl–vinyl couplings.[4] This also applies to the coupling of allyl bromides with tributyltrifluoroethenylstannane (**21**). We investigated three coupling reactions: coupling of **21** with allyl bromide **26**, cinnamyl bromide (**29**), and its isomer **30**. All reactions gave the expected (substituted) 1,1,2-trifluoropentadienes.

The coupling reactions of **21** with **26** and **29** proceeded to complete conversion with the $Pd(OAc)_2$/**13** system at room temperature and yielded less by-product than the same reaction catalyzed by $[Pd(PPh_3)_4]$, which could not be brought to completion without heating. However, reaction of **21** with **30** proceeded best with $[Pd(PPh_3)_4]$. Although there was an increase in purity of the product with **13** and a Pd compound, the reactions did not reach complete conversion.

The reactions showed an overall trend of proceeding more easily with allyl halides than with vinyl halides, and also an increase in reaction rate with decreasing fluorine substitution of the tributylvinyl tin component. For coupling reactions involving stannane **21**, a combination of a Pd salt and phosphine **13** seems to be the universal catalyst system, whereas for stannanes **20** and **19**, the choice of cocatalyst also depends on the halide used.

With most of the Stille experiments, a peculiar observation was made: during the reaction, a colorless solid was formed in the reaction vessels, in most cases crystallizing as long needles that are insoluble in all the solvents used so far. Elemental analysis of the substance is in accord with it being tributyltin fluoride. The same substance was formed when fluorovinyltributylstannanes **20** and **21** were kept at room temperature for several days or at 4 °C for several weeks.

Choice of the palladium source does not greatly influence total reaction time, but does determine the initial reaction rate at room temperature. For example, in the reaction of **21** with **24** to form **1**, $[Pd_2(dba)_3]$/**13** showed noticeable conversion after 12 h at room temperature, whereas the same ligand **13** with $Pd(OAc)_2$ did not. This difference is understandable given that $[Pd_2(dba)_3]$ already contains palladium in oxidation state zero, whereas palladium(II) in $Pd(OAc)_2$ has to be reduced by the substrate prior to the coupling reaction. This initial reduction seems to take place immediately at temperatures between 50 and 60 °C, as no coupling reaction was observed before heating to this temperature in the $Pd(OAc)_2$/**13** system. In other experiments (allyl–vinyl couplings), $Pd(OAc)_2$/**13** increased the rate of the reaction only slightly less than $[Pd_2(dba)_3]$/**13**. As this difference is of no great influence on reaction time and purity, $Pd(OAc)_2$ was chosen for all preparative experiments because it is significantly cheaper than $[Pd_2(dba)_3]$.

Table 2 summarizes the reaction conditions of the Stille coupling reactions on a preparative scale. The purity was generally higher in these experiments than in the optimization samples, as it was determined after fractional condensation under vacuum, whereby trifluoroethene and unreacted vinyl halides were removed. This explains the low yields in several reactions, in which the formation of trifluoroethene or incomplete conversion decreased the amount of isolated product (e.g., in the synthesis of **2** from **20** and **24**). The reaction of **19** with **24** did not give the desired trifluorobutadiene **4** in acceptable purity. This was to be expected from the results of the small-scale experiments, but the reason remains unclear. The yields of the optimized versus the "traditional" catalyst systems are higher in the case of **3** but lower in the case of **5**. The 1,4-dienes **9** and **10** were purified by vacuum distillation with a short Vigreux column. In the re-

Table 2. Overview of experimental conditions for the preparative experiments (Stille coupling).

Component 1 ([mmol])	Component 2 ([mmol])	Product ([mmol])	Catalyst system ([mol %])	t/T	Yield [%] (purity[a] [%])
1,3-Butadienes					
21 (13.2)	**24** (12)	**1** (8)	Pd(OAc)$_2$/**13** (0.25/ 1.25)	15 h/60 °C	75 (97)
21 (60)	**24** (50)	**1** (40)	Pd(OAc)$_2$/**13** (0.25/ 1.25)	40 h/60 °C	80 (98)
20 (9.1)	**24** (8.6)	**2** (7.8)	Pd(OAc)$_2$/**15** (0.25/ 1.25)	39 h/60 °C	35[b] (80)
20 (7.7)	**25** (7.0)	**3** (4.6)	[Pd(PPh$_3$)$_4$] (0.25)	8 h/55 °C	65 (97)
20 (16.0)	**25** (14.4)	**3** (11.3)	**32** (0.25)	8 h/60 °C	78 (95)
19 (6.8)	**24** (8.2)	**4** (3.9)	Pd(OAc)$_2$/**17** (0.31/ 1.30)	8 days/60 °C	100 (16)
19 (16.2)	**25** (14.8)	**5** (11.6)	**32** (0.25)	6 days/25 °C	78 (99)
19 (40)	**25** (38	**5** (37)	[Pd(PPh$_3$)$_4$] (1)	16 h/60 °C	98 (99)
19 (55)	**25** (50)	**5** (47)	[Pd(PPh$_3$)$_4$] (1)	23 h/60 °C	94 (99)
1,4-Dienes					
21 (15.0)	**28** (13.6)	**8** (8.9)	[Pd(PPh$_3$)$_4$] (1)	6 h/80 °C	66 (80)[c]
21 (20.0)	**29** (20.0)	**9** (3.1)	Pd(OAc)$_2$/**13** (0.25/ 1.25)	40 h/45 °C	15 (99)
21 (20.0)	**30** (20.0)	**10** (6.2)	Pd(OAc)$_2$/**13** (0.25/ 1.25)	67 h/45 °C	31 (98)

[a] With respect to by-products after distillation or fractional condensation. [b] After removal of unreacted $F_2C{=}CFBr$. [c] Product could not be separated from by-product ($H_2C{=}CHC(CH_3){=}CH_2$) by distillation.

action of **21** with **28** to form **8**, a significant amount of isoprene was formed as a by-product, most probably by β elimination from the palladium complex of halide **28**.

Negishi Coupling

Negishi coupling worked quite well for some dienes (Table 3), especially for **3**, for which the yield was even higher than with Stille coupling. The main problem is the decomposition of trifluorovinylzinc bromide during the reaction to give trifluoroethene. This leads to low yields and problems in separation, as a part of the second component may then not react. The remaining bromide or iodide was removed by condensation of the mixture of volatile components onto zinc powder in DMF to yield the nonvolatile zinc species, followed by fractional condensation under vacuum, which in turn separated solvent, product, and trifluoroethene.

Table 3. Overview of experimental conditions for the preparative experiments (Negishi coupling).

Component 1 ([mmol])	Component 2 ([mmol])	Product ([mmol])	Catalyst system ([mol %])	t/T	Yield [%] (purity[a] [%])
1,3-Butadienes					
22 (30)	**24** (20)	**1** (12)	[Pd(PPh$_3$)$_4$] (1)	24 h/75 °C	60 (97[b])
22 (30)	**25** (20)	**2** (6)	[Pd(PPh$_3$)$_4$] (1)	24 h/75 °C	30 (97[b])
23 (67)	**25** (67)	**3** (43)	[Pd(PPh$_3$)$_4$] (2.6)	4 h/75 °C	64 (99)
1,4-Dienes					
22 (15.0)	**26** (15.0)	**6** (11.2)	[Pd(PPh$_3$)$_4$] (1)	6 h/80 °C	86 (97)
22 (15.0)	**27**/**31**[e] (13.0)	**7**/**11**/**12** (6.0)	[Pd(PPh$_3$)$_4$] (1)	6 h/80 °C	38[c] (97)
22 (15.0)	**28** (13.6)	**8** (3.6)	[Pd(PPh$_3$)$_4$] (1)	6 h/80 °C	27[d] (33)

[a] With respect to by-products after fractional condensation. [b] After removal of unreacted $F_2C{=}CFBr$. [c] Both isomers **7** and **11** and by-product **12**. [d] Product could not be separated from by-product ($H_2C{=}CHC(CH_3){=}CH_2$) by distillation. [e] mixture of *E* and *Z* isomer, predominantly **27** (*E*).

As for the 1,4-dienes, the synthesis of **8** gave lower yields than with Stille coupling (27 vs. 66 %), and the problem of β elimination remains. As (*E*)-1-bromobut-2-ene (**27**) was used in only 85 % purity, the other 15 % being its *Z* isomer **31** and 2-bromo-1-butene, the pure product **7** was not to be expected but, rather, a mixture of isomers **7** and **11**. The reaction also yielded the by-product 1,1,2-trifluoro-3-ethylbutadiene (**12**), which was formed from 2-bromo-1-butene.

NMR Spectroscopy

Polyfluorinated butadienes have been the subject of some spectroscopic examinations.[42] Table 4 shows the NMR chemical shifts and coupling constants of butadienes **1**–**5**.

The ^{19}F NMR spectrum of the symmetric butadiene **1** was simulated to obtain the coupling constants of this AA′BB′CC′ spin system. Simulation of the ^{19}F NMR spectrum of **2** was performed to assign the individual signals and couplings in this complex spectrum. Both simulations were calculated by using the program g-NMR.[43] The ^{19}F{^{1}H} NMR spectrum of **3** has been published and compared with a simulated spectrum by Servis and Roberts.[42a] Their findings from 1965 could be reproduced. Trifluorovinyl groups (in **1**, **2**, and **4**) display two ^{19}F NMR signals in the range −93 to −119 ppm (terminal CF$_2$) and one at −179 to −184 ppm (CF group). The *trans*-F,F coupling constants are larger (107 to 119 Hz) than the *gem*-F,F coupling constants (51 to 70 Hz). Difluorovinyl groups (in **2**, **3**, and **5**) exhibit two signals at −78 to −89 ppm with *gem*-F,F coupling constants of 17 to 37 Hz. The ^{1}H NMR spectrum showed a signal between 4.52 and 6.24 ppm, with the central protons shifted to higher field than the terminal protons in **5** and vice versa in **4**. *trans*-H,H coupling constants are larger (17 Hz) than *cis*-H,H and CH,CH coupling constants (11 Hz), and *gem*-H,H coupling constants are too small to be observed.

Table 5 shows a selection of NMR chemical shifts and coupling constants of the 1,1,2-trifluoro-1,4-dienes **6**–**11**. The spectra are typical for trifluorovinyl-substituted compounds

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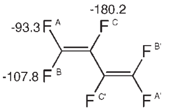
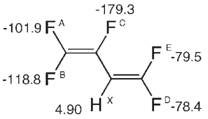
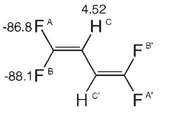
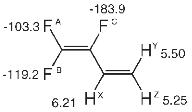
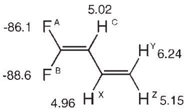
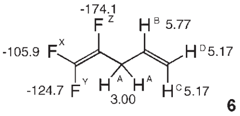
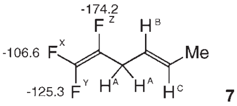
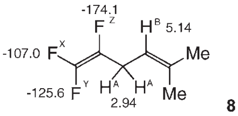
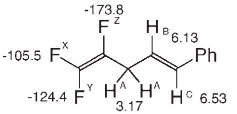
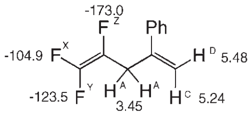
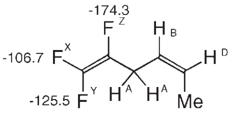
Table 4. NMR spectroscopic data for butadienes **1**–**5**.

Chemical shifts [ppm]	Coupling constants [Hz]	^{13}C chemical shifts [ppm]
 **1**	$^2J_{AB}=50.7$[a] $^3J_{BC}=118.6$[a] $^3J_{AC}=31.9$[a] $^3J_{CC'}=30.3$[a]	$\delta(C1)=\delta(C4)=152.3$ $\delta(C2)=\delta(C3)=116.0$ $\delta(C1)=155.6$ $\delta(C2)=121.8$
 **2**	$^2J_{AB}=69.8$[a] $^2J_{DE}=17.0$[a] $^3J_{AC}=31.5$[a] $^3J_{BC}=112.7$[a] $^3J_{CX}=18.0$[a] $^3J_{EX}=23.0$[a]	$\delta(C3)=70.2$ $\delta(C4)=152.6$
 **3**	$^2J_{AB}=36.6$[b] $^5J_{AA}=35.7$[b] $^3J_{AB'}=8.0$[b] $^3J_{AB'}=4.8$[b] $^3J_{CC'}=10.8$[b]	$\delta(C1)=\delta(C4)=155.6$ $\delta(C2)=\delta(C3)=72.3$
 **4**	$^2J_{AB}=64.5$ $^3J_{AC}=28.4$ $^3J_{BC}=107.1$ $^3J_{XY}=17.4$ $^3J_{XZ}=11.5$ $^3J_{CX}=25.8$	$\delta(C1)=152.6$ $\delta(C2)=128.3$ $\delta(C3)=121.0$ $\delta(C4)=114.3$
 **5**	$^2J_{AB}=26$ $^3J_{BC}=24$ $^3J_{XY}=17.2$ $^3J_{XZ}=11$ $^3J_{CX}=11$	$\delta(C1)=156.7$ $\delta(C2)=82.8$ $\delta(C3)=116.4$ $\delta(C4)=126.1$

[a] Simulation parameters. [b] As published by Servis and Roberts.[42a]

Table 5. NMR spectroscopic data of 1,4-dienes **6**–**11**.

Chemical shifts [ppm]	Coupling constants [Hz]	^{13}C chemical shifts [ppm]
 **6**	$^2J_{XY}=87.2$ $^3J_{YZ}=114.4$ $^3J_{XZ}=32.7$ $^4J_{XA}=2.7$ $^4J_{YA}=4.2$ $^3J_{ZA}=22.2$	$\delta(C1)=153.2$ $\delta(C2)=127.2$ $\delta(C3)=30.1$ $\delta(C4)=134.0$ $\delta(C5)=118.4$
 **7**	$^2J_{XY}=89.0$ $^3J_{YZ}=114.4$ $^3J_{XZ}=32.7$ $^4J_{XA}=2.7$ $^4J_{YA}=4.2$ $^3J_{ZA}=21.9$	
 **8**	$^2J_{XY}=89.8$ $^3J_{YZ}=114.1$ $^3J_{XZ}=31.9$ $^4J_{XA}=2.8$ $^4J_{YA}=4.1$ $^3J_{ZA}=22.5$	$\delta(C1)=152.9$ $\delta(C2)=128.3$ $\delta(C3)=24.8$ $\delta(C4)=116.2$ $\delta(C5)=136.2$ $\delta(Me)=25.6$ $\delta(Me)=17.7$
 **9**	$^2J_{XY}=86.8$ $^3J_{YZ}=114.5$ $^3J_{XZ}=32.6$ $^4J_{XA}=2.6$ $^4J_{YA}=4.0$ $^3J_{ZA}=21.8$	$\delta(C1)=153.2$ $\delta(C2)=127.3$ $\delta(C3)=29.3$ $\delta(C4)=121.8$ $\delta(C5)=133.5$
 **10**	$^2J_{XY}=84.7$ $^3J_{YZ}=114.5$ $^3J_{XZ}=32.8$ $^4J_{XA}=2.5$ $^4J_{YA}=4.0$ $^3J_{ZA}=21.6$	$\delta(C1)=153.6$ $\delta(C2)=127.7$ $\delta(C3)=32.0$ $\delta(C4)=140.4$ $\delta(C5)=115.4$
 **11**	$^2J_{XY}=89.0$ $^3J_{YZ}=114.4$ $^3J_{XZ}=32.5$ $^4J_{XA}=2.8$ $^4J_{YA}=4.3$ $^3J_{ZA}=21.9$	

and display nothing out of the ordinary. The three ^{19}F NMR signals of the trifluorovinyl group at −106, −124 (CF_2 group), and −175 ppm (CF group) were almost unaffected (±2 ppm) by different substituents at the other (nonfluorinated) vinyl group. This may be attributed to the double bonds in the 1,4-dienes being unconjugated, as opposed to those in the 1,3-dienes, which show a greater influence of one vinyl group on the other. The same is true for the ^{13}C NMR signals of the trifluorovinyl and the central methylene groups.

Crystal Structures

The crystal and molecular structures of dicyclohexyl-2-(1-naphthyl)phosphine, dicyclohexyl-2-(1-naphthyl)phosphine oxide, chloro(trifluoroethenyl)(tetramethylethylenediamine)zinc, and 1,1,2,4,4-pentafluorobuta-1,3-diene (**2**) were elucidated by X-ray crystallography. The crystallographic data are summarized in Table 6, and the structures are depicted in Figures 1–3.

Despite the importance of vinyl zinc derivatives in Negishi coupling reactions, there has not yet been a study of the structure of vinyl zinc compounds by X-ray crystallography so far. Chloro(trifluoroethenyl)(tetramethylethylenediamine)zinc crystallizes in the orthorhombic space group *Pna*2$_1$ with four $[Zn(Cl)(C_2F_3)(TMEDA)]$ molecules and four THF molecules in the unit cell, which does not show any short intermolecular distances. However, the refinement did not converge well. Only the carbon atom C1 exhibited unusual small thermal parameters and strange C–C and C–F distances, and the largest peak in the difference Fourier map was found very close to C1, which indicates the presence of a heavier atom close to C1. We solved this problem by assuming a disorder model with about 20% $ZnCl_2$(TMEDA) in the crystal under study. The zinc atom is almost tetrahedrally coordinated by the chloro ligand, two nitrogen atoms, and the trifluoroethenyl ligand. The C−Zn−Cl and C−Zn−N bond angles range from 108.9(2) to 112.8(2)°, whereas the angle N1−Zn1−N2 is much smaller (86.7(1)°). The zinc–carbon bond length of 1.976(7) Å lies within the distances observed for the pentafluorophenyl derivatives $[Zn(C_6F_5)_2]$ (1.926 Å)[45] and $[Zn(C_6F_5)_2(THF)_2]$ (2.012 Å).[46]

The structures of buta-1,3-diene[47] and hexafluorobuta-1,3-diene (**1**)[48] were determined by gas electron diffraction. Whereas the *anti* conformer is predominant for buta-1,3-diene[47] at all temperatures between 25 and 900 °C, hexafluorobuta-1,3-diene[48] is nonplanar with a C=C−C=C dihedral angle of 47.4°. Recently, we determined the solid-state structures of 1,1,2,-trifluorobutadiene (**4**),[49] 1,1,4,4-tetrafluorobutadiene (**3**),[21] and octafluoro-1,2-dimethylenecyclo-

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Table 6. Crystal data and structure refinement for $[Zn(Cl)(C_2F_3)TMEDA]\cdot THF$, **2**, PCy_2R (**18**), and $P(O)Cy_2R$ (R = 2-(1-naphthyl)phenyl).

	$[Zn(Cl)(C_2F_3)(TMEDA)]\cdot THF$	**2**	PCy_2R (**18**)	$P(O)Cy_2R$
Empirical formula	$ZnC_{12}H_{24}ClF_3N_2O$	$C_4H_1F_5$	$C_{28}H_{33}P$	$C_{28}H_{33}OP$
M_r	370.15	144.04	400.51	416.51
T [K]	120(2)	100(2)	143(2)	173(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	orthorhombic	orthorhombic	triclinic	monoclinic
Space group	$Pna2_1$	$Pnma$	$P\bar{1}$	$P2_1/c$
a [Å]	17.036(3)	10.638(5)	7.3867(16)	8.509(3)
b [Å]	11.019(2)	5.726(5)	8.8298(19)	25.208(9)
c [Å]	8.6158(17)	8.149(5)	18.052(4)	10.601(4)
α [°]	90	90	90.116(5)	90
β [°]	90	90	100.815(5)	90.762(9)
γ [°]	90	90	96.176(5)	90
V [Å^3]	1617.4(6)	496.4(6)	1149.5(4)	2273.8(15)
Z	4	4	2	4
ρ_{calcd} [mg m^{-3}]	1.530	1.928	1.157	1.217
μ [mm^{-1}]	1.722	0.245	0.131	0.138
F(000)	768	280	432	896
Crystal size [mm]	$0.49\times0.32\times0.08$	$1.0\times0.5\times0.5$	$0.4\times0.3\times0.1$	$0.30\times0.20\times0.06$
θ_{max} [°]	30.55°	30.5	26.37	30.61
Index ranges	$-20\leq h\leq 24$ $-15\leq k\leq 15$ $-12\leq l\leq 10$	$-15\leq h\leq 15$ $-8\leq k\leq 8$ $-11\leq l\leq 11$	$-8\leq h\leq 9$ $-11\leq k\leq 10$ $-22\leq l\leq 22$	$-12\leq h\leq 11$ $-36\leq k\leq 35$ $-10\leq l\leq 15$
Reflections collected	18958	6558	11104	27695
Independent reflections/ R_{int}	4233/0.0571	822/0.055	4671/0.047	6946/0.13
Completeness to θ_{max} [%]	99.9	100.0	99.4	99.1
Absorption correction	empirical	none	none	none
Max./min. transmission	1.0/0.82			
Refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2
Data/restraints/parameters	4233/1/181	822/0/56	4671/0/262	6946/0/271
Goodness-of-fit on F^2	1.040	1.068	1.063	1.038
$R1/wR2$ ($I>2\sigma(I)$)	0.0444/0.0950	0.066/0.184	0.051/0.1223	0.065/0.159
$R1/wR2$ (all data)	0.0734/0.1052	0.068/0.186	0.0711/0.1297	0.107/0.190
Extinction coefficient	none	0.049(15)	none	none
$\Delta\rho_{max}/\Delta\rho_{min}$ [e Å^{-3}]	0.747/−0.434	0.554/−0.555	0.371/−0.222	0.669/−0.321

TMEDA = *N,N,N′,N′*-tetramethylethylenediamine.

butane[50] by X-ray crystallography at low temperature. To establish whether the *transoid anti* conformer crystallizes for 1,1,2,4,4-pentafluorobutadiene (**2**), a single crystal was grown from the melt at −110 °C. Compound **2** crystallizes in the orthorhombic space group *Pnma* with $Z=4$. Thus, the molecule lies on the crystallographic mirror plane with C_s symmetry.

As in butadiene,[47] 1,1,2-trifluorobutadiene,[49] and 1,1,4,4-tetrafluorobutadiene,[21] the double bonds in **2** are oriented in the *transoid* form, whereas the *cisoid* form is only observed in the presence of steric constraints such as in octafluoro-1,2-dimethylenecyclobutane,[50] 2,3,5,6,7,8-hexamethylenebicyclo[2.2.2]octane,[51] or upon coordination to a metal center like in $[Fe(CO)_3(\eta^4\text{-}C_4H_6)]$.[52] Both C−C double-bond lengths are almost equal (C1−C2 1.320(3), C3−C4 1.318(3) Å), which shows a negligible influence of fluorine substitution on the C−C bond lengths, in agreement with our earlier results found for 1,1,2-trifluorobutadiene[49] and the C−C bond lengths obtained from low-temperature X-ray diffraction of ethane[53] and tetrafluoroethene.[54] On the basis of ab initio calculations, the C−C bond lengths of ethane[55] and tetrafluoroethene[56] differ by 0.007 Å on the MP2 level of theory with the 6-31G** basis set.

The central carbon–carbon bond C2−C3 (1.435(3) Å) is shortened due to conjugation effects, in contrast to the structure of 2,3-di-*tert*-butylbuta-1,3-diene,[57] which has a long central bond of 1.506(3) Å and a C=C−C=C torsion angle of 96.6°. Alternating bond lengths (1.336, 1.451, 1.327, and 1.451 Å) with single bonds shortened due to conjugation were found in *trans,trans*-1,3,5,7-octatetraene,[58] which has torsion angles of 179.3 and 179.9°. The C−F bond lengths of the CF_2 group is considerably shorter than in the CF group, an effect already observed for other fluoro alkenes such as trifluoroethene,[56] 1,1-difluoroethene,[56] (*E*)- and (*Z*)-1,2-difluoroethene,[56] hexafluoropropene,[59] and 1,1,2-trifluorobutadiene.[49] The F−C−F bond angle of 111.7(2)° is similar to that in 1,1,2-trifluorobutadiene,[49] 1,1,4,4-tetrafluorobutadiene,[21] and hexafluoropropene.[59] The C−C−C bond angle at C2 is slightly larger than that at C3. The bond lengths and angles of **2** are summarized in Table 7.

Figure 2 shows the packing of **2** along the *b* axis. The short intermolecular H···F contacts (H3···F3 2.43 Å; C−H

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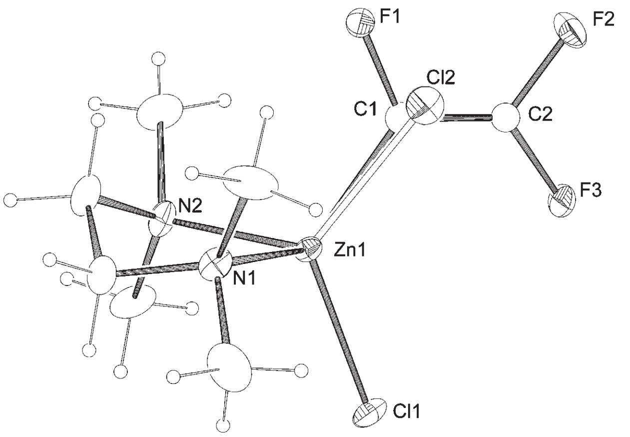

Figure 1. ORTEP drawing[44] of the molecular structure of chloro(trifluoroethenyl)(tetramethylethylenediamine)zinc (solvate molecule omitted). Ellipsoids are drawn at the 50 % probability level.

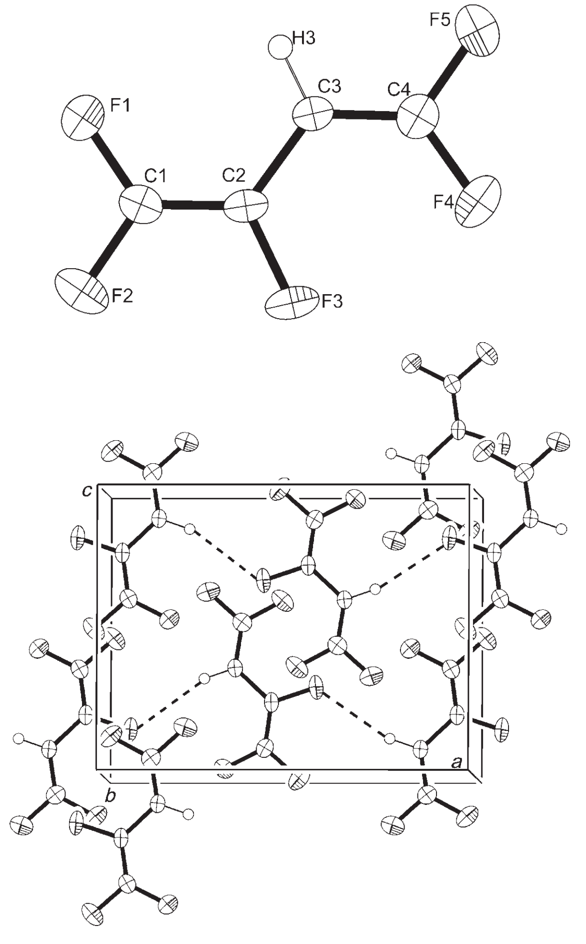

Figure 2. ORTEP drawings[44] of the molecular structure (top) and packing diagram (bottom) of 1,1,2,4,4-pentafluorobutadiene (**2**). Ellipsoids are drawn at the 50 % probability level.

bonds normalized to 1.08 Å[60]) connect molecules within the crystallographic mirror plane to form chains along the *a* axis.

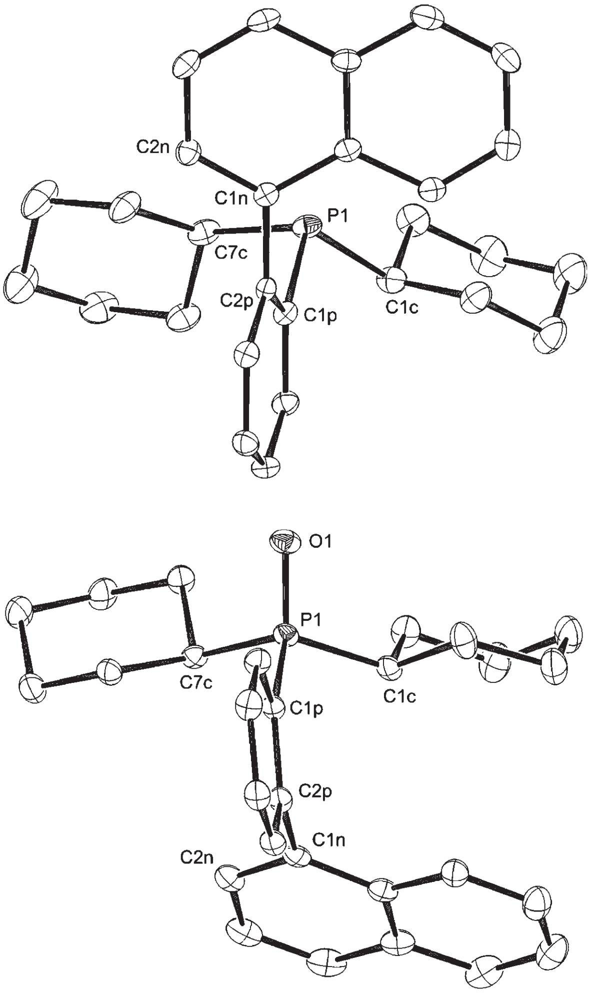

Figure 3. ORTEP drawings[44] of the molecular structures of dicyclohexyl-2-(1-naphthyl)phenylphosphine (**18**; top) and dicyclohexyl-2-(1-naphthyl)phosphine oxide (bottom) (hydrogen atoms omitted for clarity). Ellipsoids are drawn at the 50 % probability level.

The molecular structures of dicyclohexyl-(2-(1-naphthyl)-phenyl)phosphine **18** and dicyclohexyl-(2-(1-naphthyl)phenyl)phosphine oxide are depicted in Figure 3. Crystals of **18** were obtained by recrystallization from ethyl acetate. One of the crystallization attempts yielded crystals of dicyclohexyl-(2-(1-naphthyl)phenyl)phosphine oxide when the sample was accidentally left to stand in air for several days. Major differences between the structures of the two compounds can be found in the conformation of the 2-(1-naphthyl)phenyl substituent, the P–C bond lengths, and the C–P–C bond angles. As expected, the P–C bond lengths decreased and the C–P–C bond angles increased in going from the phosphine to the phosphine oxide. In the phosphine, the naphthalene ring is oriented more or less parallel to the lone-pair electrons of the phosphorus atom, whereas in the phosphine oxide, the naphthalene ring is at the maximum distance from the oxygen atom.

Table 7. Bond lengths and angles for 1,1,2,4,4-pentafluorobutadiene.

Bond	Length [Å]	Bond angle	Angle [°]
C1–F1	1.310(2)	F1–C1–C2	124.84(17)
C1–C2	1.320(3)	F1–C1–F2	111.66(17)
C1–F2	1.320(2)	C2–C1–F2	123.50(18)
C2–F3	1.350(2)	C1–C2–F3	116.48(17)
C2–C3	1.435(3)	C1–C2–C3	125.27(17)
C3–C4	1.318(3)	F3–C2–C3	118.25(18)
C3–H3	0.9300	C4–C3–C2	124.62(19)
C4–F4	1.311(2)	C4–C3–H3	117.7
C4–F5	1.315(2)	C2–C3–H3	117.7
		F4–C4–F5	109.75(17)
		F4–C4–C3	126.94(19)
		F5–C4–C3	123.31(19)

Conclusions

Our experiments have demonstrated that fluorinated 1,3-butadienes can be easily obtained in good yields by palladium-catalyzed C–C coupling reactions with readily available transmetalation reagents. These can be prepared in high yield from inexpensive starting materials such as hfc-134a and hcfc-142b. Furthermore, the amount of palladium catalyst used can be decreased to 0.25 mol % by using special ligand systems. There exists an easier, copper-catalyzed route to fluorinated 1,4-dienes that gave comparable yields of **6**.[16]

It should be possible to transfer these reactions to more-complicated systems, thus facilitating the introduction of difluoro- and trifluorovinyl groups into molecules of interest in life-science applications, preferentially with zinc reagents, as tin-containing impurities (which are very toxic) cannot be removed easily. The room-temperature preparation of trifluoroethenyl zinc chloride from 1,1,1,2-tetrafluoroethane reported by Raghavanpillai and Burton[33,39] may be particularly useful for these applications, as the separation of highly volatile by-products is not a problem in this case.

Experimental Section

General

All reactions were carried out under dry argon by using standard Schlenk and vacuum techniques. Volatile materials were handled in a conventional glass vacuum line, and amounts were determined by PVT techniques. Moisture-sensitive compounds were handled in an automatic dry box (Braun) under dry argon. ^{1}H, ^{13}C, ^{19}F, ^{31}P, and ^{119}Sn NMR spectra were recorded on a JEOL FX 90Q or JEOL LAMBDA 400 instrument with tetramethylsilane (TMS) (^{1}H, ^{13}C) or solvent signals (^{19}F: $CFCl_3$; ^{31}P: H_3PO_4) as standards. Infrared spectra were recorded on a SHIMADZU FT-IR8400S (gas samples in a 10-cm cuvette with KBr windows) instrument. Raman spectra were recorded on a Bruker RFS 100 instrument. Mass spectra were obtained on a Varian MAT 711 (80 eV) spectrometer.

DMF was dried over calcium hydride. Bromotrifluoroethene and 1,1-difluoroethene were purchased from Fluorochem or Fluka and were used as supplied. 1,1,1,2-Tetrafluoroethane and 1-chloro-2,2-difluoroethane (hfc-134a/142b, coolant grade) were generously provided by Solvay Fluor und Derivate GmbH. They were used without purification.

Tetrakis(triphenylphosphanyl)palladium was prepared by the method of Coulson.[61] Dicyclohexyl-2-(2′-methylbiphenyl)phosphine (**13**), dicyclohexyl-2-(2′,6′-dimethoxybiphenyl)phosphine (**16**), dicyclohexyl-2-(2′,4′,6′-trimethylbiphenyl)phosphine (**14**), and dicyclohexyl-2-(1-naphthyl)phosphine (**18**) were prepared by the method of Buchwald and co-workers.[40] A quantity of **13**, dicyclohexyl-2-(2′,4′,6′-triisopropylbiphenyl)phosphine (**15**), and dicyclohexyl-2-(2′-(*N*,*N*-dimethylamino)biphenyl)phosphine (**17**) was generously provided by Lanxess AG. Tributylethenylstannane was prepared by the method of Casado and Espinet.[62] Palladium acetate was purchased from ChemPur or Merck. Cinnamyl bromide and tributylchlorostannane were obtained from Acros, and allyl bromide was taken from institute stocks.

Coupling reactions were carried out either by Negishi or Stille methods. We developed four standard procedures. The choice of the procedure for a given reaction depended on the boiling point of the product (separation from the solvent and by-products).

Negishi Reactions

Procedure 1: The reactions were carried out in an all-glass apparatus consisting of two 100-mL flasks connected by a glass frit and equipped with polytetrafluoroethene (PTFE) valves and magnetic stirrer bars in both flasks. The vinyl halide was condensed onto a twofold excess of activated zinc dust in DMF. The mixture was allowed to warm. At slightly below room temperature, an exothermic reaction started, which converted the halide into the zinc reagent (component 1). The mixture turned brown and warmed to 50–60 °C. When the exothermic reaction was considered too vigorous, the reaction vessel was cooled in an ice bath for some minutes. The mixture was stirred at 60 °C for another 2 h. Upon cooling to room temperature, a sample of the gas phase was pumped off to check for remains of component 1 by IR spectroscopy. The solution of trifluoroethenylzinc bromide was then filtered through the frit into the second flask, to which tetrakis(triphenylphosphanyl)palladium (1–2 mol %) had been added. The second flask was sealed off from the rest of the apparatus to prevent the vinyl or allyl halide added in the next step (component 2) from reacting with the excess of zinc dust. Component 2 was condensed onto the reaction mixture, and upon warming to room temperature, the second flask was heated in an oil bath for 6–24 h. The products where purified by fractional condensation under vacuum (10^{-2} mbar), with the solvent left in a cold trap kept at −40 °C, the respective products in a second trap kept at −100 to −130 °C, and the volatile by-product (trifluoroethene) in a trap cooled with liquid nitrogen.

Procedure 2: In a dried flask equipped with a septum, a magnetic stirrer bar, and an argon inlet, activated zinc powder was suspended in dry DMF. Bromotrifluoroethene was condensed onto the solvent at liquid-nitrogen temperatures. The mixture was allowed to warm to room temperature, at which point an exothermic reaction started, turning the mixture dark brown. The solution was then transferred through a PTFE tube into a Schlenk tube containing the palladium catalyst and component 2 in dry DMF; the excess of zinc dust was left in the first flask. The tube was cooled with liquid nitrogen, evacuated, and heated to 80 °C for 6 h. The products were isolated by fractional condensation.

Stille Reactions

Stille reactions were carried out in flasks or tubes equipped with PTFE valves and magnetic stirrer bars.

Procedure 3 used for the preparation of volatile dienes: Component 2 was condensed onto a mixture of component 1 (tin reagent) and the palladium catalyst (0.25–1.5 mol %) in DMF. The mixture was warmed to room temperature and stirred for 2–200 h at 60–80 °C in an oil bath. The products were purified by trap-to-trap distillation, with the solvent left in a trap at −40 °C, the product in a second trap at −100 to −120 °C, and the by-product (trifluoroethene or 1,1-difluoroethene) in a trap cooled with liquid nitrogen.

Procedure 4 used for Stille reactions with nonvolatile products (with respect to solvent or by-products): Components 1 and 2 and the catalyst were dissolved in DMF and then treated as described above. The products were isolated by aqueous workup followed by vacuum distillation or fractional condensation.

Typical procedure for the optimization of the Stille reactions: Tributyltrifluoroethenylstannane (408 mg, 1.1 mmol), a dicyclohexylphosphane, and

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a palladium compound were placed in a dried tube (external diameter 8 mm, about 4.5 mL internal volume), and dry DMF (1 mL) was added. The mixture was cooled with liquid nitrogen, argon was pumped off, and the mixture was warmed to room temperature, cooled again, and evacuated to remove the last traces of oxygen. Next, bromotrifluoroethene (162 mg, 1.0 mmol) was condensed onto the mixture, and the tube was sealed. It was allowed to warm to room temperature and left overnight. A ^{19}F NMR spectrum was recorded on a JEOL FX-90 spectrometer with the reaction vessel in a 10-mm sample tube. Over the following days, the vessel was repeatedly heated in an oil bath or oven for several hours before more ^{19}F NMR spectra were recorded to monitor the progress of the reaction. The reaction was considered complete when the peaks of one of the initial compounds had disappeared. A catalyst system was found to be best when short reaction times could be combined with low reaction temperatures, small amounts of by-products, and the total conversion of starting material. The most promising catalyst system was then used in a larger-scale experiment, in which the product was isolated to determine the yield.

Details and Spectroscopic Data

Tributyl-(2,2-difluoroethenyl)stannane, method A (from 1,1-difluoroethene): In a 500-mL flask equipped with a dropping funnel, a septum, an argon inlet, and a magnetic stirrer bar, a mixture of dry THF and dry diethyl ether (4:1, 200 mL) was cooled to −196 °C. 1,1-Difluoroethene (3.05 g, 47.6 mmol) was condensed onto the solvent after evacuation of the flask. The temperature was increased to −110 °C, the flask was filled with argon and equipped with a bubbler, and *sec*-butyllithium (36 mL, 1.3 M solution in hexane/cyclohexane (92:8), 46.8 mmol) was added over 45 min with a syringe. The solution was stirred at −100 °C for another hour. Tributylchlorostannane (13.13 g, 40.4 mmol) was added over 45 min through the dropping funnel. The solution was allowed to warm to room temperature overnight while a slow stream of argon was maintained through the flask to remove traces of fluoroacetylene, which was formed from 2,2-difluorovinyllithium in the case of local overheating (temperatures greater than −90 °C). In the morning, the solution had turned dark brown. The solvent was evaporated, and the residue was dissolved in diethyl ether and washed with brine. The organic phase was passed over a short column of silica gel. After evaporation of diethyl ether, the product was distilled under high vacuum (b.p.: 46 °C (0.4 Pa), 11.41 g, 32.9 mmol, 78 %). NMR spectroscopy of the distillate showed no other compounds present.

Tributyl-(2,2-difluoroethenyl)stannane, method B (from 1-chloro-1,1-difluoroethane): 1-Chloro-1,1-difluoroethane (6.08 g, 60.5 mmol) was treated with slightly less than 2 equivalents of *sec*-butyllithium (77 mL, 1.4 M solution in hexane/cyclohexane (92:8), 108 mmol) at −110 °C in the solvent mixture (200 mL) described in method A. Internal measurement of the temperature was essential to avoid decomposition by control of the rate of addition of *sec*-butyllithium. Tributylchlorostannane (16.20 g, 49.8 mmol) was added to this solution of 2,2-difluorovinyllithium over 25 min. After workup similar to that in method A, distillation yielded the pure product (13.49 g, 38.2 mmol, 77 %). Repeated experiments gave yields between 66 and 82 %.

Tributyl-(2,2-difluoroethenyl)stannane: ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C, TMS): $\delta=3.87$ (dd, ^{3}J(H,*trans*-F) = 47.5 Hz, ^{3}J(H,*cis*-F) = 9.8 Hz, 1 H; CH), 1.62–1.40 (m, 6 H; CH_2), 1.38–1.28 (m, 6 H; CH_2), 0.98 (t, ^{3}J(H,H) = 8 Hz, 6 H; CH_2), 0.86 ppm (t, ^{3}J(H,H) = 8 Hz, 9 H; CH_3); ^{13}C{^{1}H} NMR (100.4 MHz, $CDCl_3$, 21 °C, TMS): $\delta=157.8$ (dd, ^{1}J(C,F) = 277, 311 Hz; CF_2), 63.3–64.2 (m; CH), 29.9 (s, Sn satellites = 11 Hz; CH_2 (γ-Sn)), 27.2 (s, Sn satellites = 30 (^{119}Sn), 28 Hz (^{117}Sn); CH_2(β-Sn)), 13.6 (s; CH_3), 10.0 ppm (s, Sn satellites = 182 (^{119}Sn), 174 Hz (^{117}Sn); CH_2(α-Sn)); ^{19}F NMR (376 MHz, $CDCl_3$, 21 °C, $CFCl_3$): $\delta=-61.3$ (dd, ^{2}J(F,F) = 36.7 Hz, ^{3}J(F,H) = 9.8 Hz, 1 F; CF_2), −73.4 ppm (dd, ^{3}J(F,H) = 47.5 Hz, ^{2}J(F,F) = 36.7 Hz, 1 F; CF_2); MS (70 eV, EI): *m/z* (%) = 354 (2) $[M]^+$, 297 (100) $[M-C_4H_9]^+$, 253 (98), 213 (21), 197 (13), 177 (31), 139 (22), 121 (14), 103 (7), 57 (38) $[C_4H_9]^+$, 41 (49) $[C_3H_7]^+$, 29 (64) $[C_2H_5]^+$ (spectroscopic data in accordance with those in reference [31]).

Tributyl(trifluoroethenyl)stannane: The method of Burdon et al.[32] was used with some modifications. 1,1,1,2-Tetrafluoroethane (14.5 g, 142 mmol) was condensed onto dry THF (200 mL) in a three-necked 1000-mL flask cooled with liquid nitrogen. The mixture was warmed to −78 °C in a dry ice/ethanol bath. Under argon, *n*-butyllithium (88 mL, 2.5 M solution in hexane, 220 mmol) was added over 30 min. After 1 h of stirring at −78 °C, tributylchlorostannane (32.5 g, 100 mmol) in dry THF (80 mL) was added over 45 min. The mixture was allowed to warm to room temperature overnight. THF and hexane were evaporated, and the residue was dissolved in dichloromethane and extracted with water. The organic phase was dried over magnesium sulfate. After evaporation of the solvent, the crude product was distilled under high vacuum (b.p.: 62 °C (0.2 Pa)) to yield pure tributyl(trifluoroethenyl)stannane (28.9–35.2 g, 77.9–94.8 mmol, 78–95 %). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C, TMS): $\delta=1.53$ (tt, ^{3}J(H,H) = 7, 8 Hz, 6 H; CH_2(γ-Sn)), 1.32 (tq, ^{3}J(H,H) = 7.3, 6 Hz; CH_2(β-Sn)), 1.08 (t, ^{3}J(H,H) = 8 Hz, ^{2}J(H,Sn) = 27 Hz, 6 H; CH_2(α-Sn)), 0.89 ppm (t, ^{3}J(H,H) = 7.3 Hz, 9 H; CH_3); ^{13}C{^{1}H} NMR (100.4 MHz, $CDCl_3$, 22 °C, TMS): $\delta=161.5$ (td, ^{1}J(C,F) = 268 Hz, ^{2}J(C,F) = 35 Hz; CF_2), 133.1 (d, ^{1}J(C,F) = 205 Hz; CF), 28.6 (s, Sn satellites = 11 Hz; CH_2(γ-Sn)), 27.0 (s, Sn satellites = 31 (^{119}Sn), 29 Hz (^{117}Sn); CH_2(β-Sn)), 13.5 (s; CH_3), 9.8 ppm (s, Sn satellites = 182 (^{119}Sn), 175 Hz (^{117}Sn); CH_2(α-Sn)); ^{13}C{^{19}F} NMR (100.4 MHz, $CDCl_3$, 22 °C, TMS): $\delta=$ 161.5 (s; CF_2), 133.1 (s; CF), 28.6 (t, ^{1}J(C,H) = 120 Hz; CH_2(γ-Sn)), 27.0 (t, ^{1}J(C,H) = 133 Hz; CH_2(β-Sn)), 13.5 (q, ^{1}J(C,H) = 126 Hz; CH_3), 9.8 ppm (t, ^{1}J(C,H) = 127 Hz; CH_2(α-Sn)); ^{19}F NMR (376 MHz, $CDCl_3$, 22 °C, $CFCl_3$): $\delta=-88.5$ (dd, ^{3}J(F,F) = 72 Hz, ^{3}J(F,F) = 34 Hz, 1 F; CF_2), −123.1 (dd, ^{3}J(F,F) = 115 Hz, ^{3}J(F,F) = 72 Hz, 1 F; CF_2), −193.2 ppm (dd, ^{3}J(F,F) = 115 Hz, ^{3}J(F,F) = 34 Hz, 1 F; CF_2); MS (70 eV, EI): *m/z* (%) = 372 (5) $[M]^+$, 315 (100) $[M-C_4H_9]^+$, 291 (2) $[M-C_2F_3]^+$, 259 (61) $[M-2C_4H_9]^+$, 201 (40) $[M-3C_4H_9]^+$, 177 (8) $[M-C_2F_3-2C_4H_9]^+$, 139 (10) $[SnC_4H_8]^+$, 121 (8) $[SnH]^+$, 57 (33) $[C_4H_9]^+$, 41 (49) $[C_3H_7]^+$ (spectroscopic data in accordance with those in reference [32]).

2,2-Difluoroiodoethene: 1-Chloro-1,1-difluoro-2-iodoethane (17.9 g, 79.2 mmol) was condensed onto *tert*-butanol (200 mL). The mixture was warmed to room temperature. Potassium *tert*-butylate (9.34 g, 83.1 mmol in 100 mL *tert*-butanol) was added to the stirred solution while room temperature was maintained by using a water bath. The product was condensed under high vacuum into a trap cooled with liquid nitrogen through a trap at −55 °C, which held back *tert*-butanol. Fractional condensation had to be repeated once, then pure 2,2-difluoroiodoethene was obtained in the second trap (9.35 g, 49.2 mmol, 62 %). IR (gas): $\tilde{\nu}=3126$, 3117, 2662, 2270, 1726, 1717, 1700, 1469, 1317, 1308, 1144, 1136, 953, 946, 747, 738, 731 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C, TMS): $\delta=$ 4.82 ppm (dd, ^{3}J(H,F) = 22.8 Hz, ^{3}J(H,F) = 2.1 Hz; CH); ^{13}C{^{1}H} NMR (100.4 MHz, $CDCl_3$, 22 °C, TMS): $\delta=156.5$ (dd, ^{1}J(C,F) = 295.5 Hz, ^{1}J(C,F) = 285.5 Hz; CF_2), 24.2 ppm (dd, ^{2}J(C,F) = 37.0 Hz; ^{2}J(C,F) = 29.2 Hz; CHI); ^{13}C{^{19}F} NMR (100.4 MHz, $CDCl_3$, 22 °C, TMS): $\delta=156.5$ (d, ^{2}J(C,H) = 4.5 Hz; CF_2), 24.1 ppm (d, ^{1}J(C,H) = 296.5 Hz; CHI); ^{19}F NMR (376 MHz, $CDCl_3$, 22 °C, $CFCl_3$): $\delta=-71.4$ (dd, ^{2}J(F,F) = 26.2 Hz, ^{3}J(F,H) = 2.1 Hz; CF_2), −75.8 ppm (dd, ^{2}J(F,F) = 26.2 Hz, ^{3}J(F,H) = 23.6 Hz; CF_2).

Hexafluorobutadiene (procedures 1 and 3): IR (gas): $\tilde{\nu}=1794$, 1767, 1329, 1190, 1142, 1136, 968 cm^{-1} (spectroscopic data in accordance with those in reference [42c]); ^{13}C{^{19}F} NMR (100.4 MHz, $CDCl_3$, 20 °C, TMS): $\delta=116.0$ ppm (s; CF), 152.3 (s; CF_2); ^{19}F NMR (376 MHz, $CDCl_3$, 20 °C, $CFCl_3$): $\delta=-93.1$ to −93.4 (m, 2 F; CF_2), −107.5 to −108.1 (m, 2 F; CF_2), −179.9 to −180.5 ppm (m, 2 F; CF).

1,1,2,4,4-Pentafluorobutadiene (procedures 1 and 3): Stille coupling of tributyltrifluoroethenylstannane with 2,2-difluoroiodoethene gave substantial amounts of hexafluorobutadiene as a by-product, which could not be separated from the product. This problem did not occur in the Stille reaction of tributyl-(2,2-difluoroethenyl)stannane with bromotrifluoroethene. The Negishi reaction also yielded some symmetrical dienes when part of the excess of zinc dust was transferred to the second reaction vessel, which led to a mixture of zinc reagents. M.p.: 163 K (0.1 MPa); b.p.: 292 K (determined from measurement of the vapor-pressure curve); IR (gas): $\tilde{\nu}=1790$, 1728, 1389, 1323, 1300, 1246, 1184, 1146, 1084, 935, 845, 789 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C, TMS): $\delta=$ 4.82–5.00 ppm (m); ^{13}C NMR (100.4 MHz, $CDCl_3$, 20 °C, TMS): $\delta=$ 152.5–158.8 (m), 149.7–155.3 (m), 121.0–122.6 (m), 69.7–70.6 ppm (m);

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^{19}F NMR (376 MHz, CDCl$_3$, 20 °C, CFCl$_3$): $\delta=-179.1$ to -179.5 (m, 1F; CF), -118.5 to -119.1 (m, 1F; CF$_2$), -101.7 to -102.1 (m, 1F; CF$_2$), -79.4 to -79.5 (m, 1F; CF$_2$), -78.2 to -78.5 ppm (m, 1F; CF$_2$).

1,1,4,4-Tetrafluorobutadiene (procedure 3): The preparation of 1,1,4,4-tetrafluorobutadiene by the Negishi reaction of **23** with **25** was reported in reference [21] to reach a yield of 66 %. IR (gas): $\tilde{\nu}=3122$, 1740, 1715, 1321, 1172, 1140, 949, 922, 826, 739, 548 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$, 22 °C, TMS): $\delta=4.45$–4.59 ppm (m, 1H; CH); ^{13}C{^{1}H} NMR (100.4 MHz, CDCl$_3$, 20 °C, TMS): $\delta=152.6$–158.7 (m; CF$_2$), 72.0–72.6 ppm (m; CH); ^{19}F NMR (376 MHz, CDCl$_3$, 20 °C, CFCl$_3$): $\delta=-86.7$ to -86.9 (m, 1F; CF$_2$), -87.9 to -88.3 ppm (m, 1F; CF$_2$).

1,1,2-Trifluorobutadiene (procedure 3): IR (gas): $\tilde{\nu}=1761$, 1344, 1334, 1286, 1101, 979, 916 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$, 22 °C, TMS): $\delta=6.21$ (ddddd, ^3J(H,F) = 25.8 Hz, ^3J(H,*trans*-H) = 17.4 Hz, ^3J(H,*cis*-H) = 11.5 Hz, ^4J(H,F) = 3.6, 1.7 Hz, 1H; CH), 5.47–5.52 (m, 1H; CH$_2$), 5.23–5.27 ppm (m, 1H; CH$_2$); ^{13}C{^{1}H} NMR (100.4 MHz, CDCl$_3$, 23 °C, TMS): $\delta=152.6$ (ddd, ^1J(C,F) = 294, 283 Hz, ^2J(C,F) = 45 Hz; CF$_2$), 126.8–129.8 (m; CF), 121.0 (dd, ^2J(C,F) = 19 Hz, ^3J(C,F) = 5.4 Hz; CH), 114.2–114.4 ppm (m; CH$_2$); ^{13}C{^{19}F} NMR (100.4 MHz, CDCl$_3$, 23 °C, TMS): $\delta=152.4$ (s; CF$_2$), 128.0 (s; CF), 120.9 (dt, ^1J(C,H) = 162 Hz, ^2J(C,H) = 3.8 Hz; CH), 114.1 ppm (td, ^1J(C,H) = 162 Hz, ^2J(C,H) = 2.9 Hz; CH$_2$); ^{19}F NMR (376 MHz, CDCl$_3$, 23 °C, CFCl$_3$): $\delta=-103.3$ (dd, ^2J(F,F) = 64.5 Hz, ^3J(F,F) = 28.4 Hz, 1F; CF$_2$), -119.2 (ddd, ^3J(F,F) = 107.1 Hz, ^2J(F,F) = 64.5 Hz, ^4J(F,H) = 1.5 Hz, 1F; CF$_2$), -183.9 ppm (dddd, ^3J(F,*trans*-F) = 107.1 Hz, ^3J(F,F) = 28.4 Hz, ^3J(F,H) = 25.6 Hz, ^4J(F,H) = 1.4 Hz, 1F; CF).

5: 1,1-Difluorobutadiene: 2,2-Difluoroiodoethene was prepared as described above (in earlier experiments according to reference [27]). This compound was coupled with stannane **19** (procedure 3) to yield **5**. IR (gas): $\tilde{\nu}=3106$ (C–H), 1734, 1731, 1725, 1437, 1425, 1339, 1337, 1215, 1210, 1203, 990, 904, 895, 801 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$, 24 °C, TMS): $\delta=6.24$ (ddddd, ^3J(H,*trans*-H) = 17.2 Hz, ^3J(H,*cis*-H) = 11 Hz, ^3J(H,H) = 11 Hz, ^4J(H,F) = 1, 1 Hz, 1H; =CH$_2$), 5.07–5.23 (m, 1H; =CH), 5.01–5.03 (m, 1H, =CH$_2$), 4.91–5.00 ppm (m, ^3J(H,*trans*-F) = 24 Hz, 1H; CH=); ^{13}C{^{1}H} NMR (100.4 MHz, CDCl$_3$, 24 °C, TMS): $\delta=156.7$ (dd, ^1J(C,F) = 296.5, 290.7 Hz, C1), 126.1 (dd, ^4J(C,F) = 5.0, 1.3 Hz, C4), 116.4 (dd, ^3J(C,F) = 11.0, 2.7 Hz, C3), 82.8 ppm (dd, ^2J(C,F) = 26.7, 16.8 Hz, C2); ^{19}F NMR (376 MHz, CDCl$_3$, 24 °C, CFCl$_3$): $\delta=-86.1$ (dd, ^2J(F,F) = 26 Hz, ^3J(F,*trans*-H) = 24 Hz, 1F, F$_2$C=), -88.6 ppm (d, ^2J(F,F) = 26 Hz, 1F, F$_2$C=).

1,1,2-Trifluoropenta-1,4-diene (procedures 3 and 2): IR (gas): $\tilde{\nu}=3096$, 3025, 2997, 2919, 1801, 1652, 1646, 1436, 1431, 1430, 1424, 1304, 1267, 1218, 1141, 1105, 1072, 993, 929, 923, 792 cm^{-1} (spectroscopic data in accordance with those in reference [16]); ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C, TMS): $\delta=5.77$ (ddt, ^3J(H,*trans*-H) = 16.9 Hz, ^3J(H,*cis*-H) = 10.4 Hz, ^3J(H,H) = 6.2 Hz, 1H; CH), 5.12–5.22 (m, 2H; CH$_2$), 2.97–3.03 ppm (m, 2H; CH$_2$); ^{13}C{^{1}H} NMR (100.4 MHz, CDCl$_3$, 21 °C, TMS): $\delta=153.2$ (ddd, ^1J(C,F) = 286.2, 270.4 Hz, ^2J(C,F) = 46.3 Hz; CF$_2$), 134.0 (s; CH) 127.2 (ddd, ^1J(C,F) = 235.3 Hz, ^2J(C,F) = 53.0, 15.8 Hz; CF), 118.4 (s, CH$_2$), 30.1 ppm (dd, ^3J(C,F) = 22.3 Hz, ^4J(C,F) = 2.5 Hz; CH$_2$); ^{19}F NMR (376 MHz, CDCl$_3$, 19 °C, CFCl$_3$): $\delta=-105.9$ (ddt, ^2J(F,F) = 87.2 Hz, ^3J(F,*cis*-F) = 32.7 Hz, ^4J(F,H) = 2.7 Hz, 1F; CF$_2$), -124.7 (ddt, ^3J(F,*trans*-F) = 114.4 Hz, ^2J(F,F) = 87.2 Hz, ^4J(F,H) = 4.2 Hz, 1F; CF$_2$), -174.1 ppm (ddt, ^3J(F,*trans*-F) = 114.4, ^3J(F,*cis*-F) = 32.7 Hz, ^3J(F,H) = 22.2 Hz, 1F; CF).

1,1,2-Trifluorohexa-1,4-diene: A mixture of *E* and *Z* isomers was formed by Negishi coupling as the allyl component isomerises above room temperature. From an impurity (2-bromo-1-butene), 1,1,2-trifluoro-3-ethylbuta-1,3-diene (**12**) was formed as a by-product (≈5 %). The products were not separated. *E* isomer (**7**): ^{19}F NMR (376 MHz, CDCl$_3$, 20 °C, CFCl$_3$): $\delta=-106.6$ (ddt, ^2J(F,F) = 89.0 Hz, ^3J(F,*cis*-F) = 32.5 Hz, ^4J(F,H) = 2.8 Hz, 1F; CF$_2$), -125.3 (ddt, ^3J(F,*trans*-F) = 114.4 Hz, ^2J(F,F) = 89.0 Hz, ^4J(F,H) = 4.2 Hz, 1F; CF$_2$), -174.2 ppm (ddt, ^3J(F,*trans*-F) = 114.4 Hz, ^3J(F,*cis*-F) = 32.5 Hz, ^3J(F,H) = 21.9 Hz, 1F; CF). *Z* isomer (**11**): ^{19}F NMR (376 MHz, CDCl$_3$, 20 °C, CFCl$_3$): $\delta=-106.7$ (ddt, ^2J(F,F) = 89.0 Hz, ^3J(F,*cis*-F) = 32.5 Hz, ^4J(F,H) = 2.8 Hz, 1F; CF$_2$), -125.5 (ddt, ^3J(F,*trans*-F) = 114.4 Hz, ^2J(F,F) = 89.0 Hz, ^4J(F,H) = 4.3 Hz, 1F; CF$_2$), -174.3 ppm (ddt, ^3J(F,*trans*-F) = 114.4 Hz, ^3J(F,*cis*-F) = 32.5 Hz, ^3J(F,H) = 21.9 Hz, 1F; CF).

12: 1,1,2-Trifluoro-3-ethylbuta-1,3-diene: ^{19}F NMR (376 MHz, CDCl$_3$, 20 °C, CFCl$_3$): $\delta=-106.7$ (dd, ^2J(F,F) = 89.0 Hz, ^3J(F,*cis*-F) = 32.5 Hz, 1F; CF$_2$), -123.4 (ddd, ^3J(F,*trans*-F) = 113.7 Hz, ^2J(F,F) = 89.0 Hz, ^4J(F,H) = 3.5 Hz, 1F, CF$_2$), -183.1 ppm (ddd, ^3J(F,*trans*-F) = 113.7 Hz, ^3J(F,*cis*-F) = 32.5 Hz, ^3J(F,H) = 29.6 Hz, 1F; CF).

8: 1,1,2-Trifluoro-5-methylhexa-1,4-diene (procedures 2 and 3): Stille coupling gave better results than Negishi coupling with this diene. With both methods, the product contained some isoprene as a by-product, which was formed by β-H elimination from the Pd complex of **28**. ^{1}H NMR (400 MHz, CDCl$_3$, 19 °C, TMS): $\delta=5.11$–5.17 (m, 1H; CH), 2.88–2.99 (m, 2H; CH$_2$), 1.72 (d, ^4J(H,H) = 1.1 Hz, 3H; CH$_3$), 1.64 ppm (s, 3H; CH$_3$); ^{13}C{^{1}H} NMR (100.4 MHz, CDCl$_3$, 21 °C, TMS): $\delta=152.9$ (ddd, ^1J(C,F) = 285.8, 271.7 Hz, ^2J(C,F) = 47.2 Hz; CF$_2$), 136.2 (s; C$_{\text{tert}}$) 128.3 (ddd, ^1J(C,F) = 234.9 Hz, ^2J(C,F) = 52.2, 14.9 Hz; CF), 116.2 (s, CH), 25.6 (s; CH$_3$), 24.8 (dd, ^3J(C,F) = 22.4 Hz, ^4J(C,F) = 2.1 Hz; CH$_2$), 17.7 ppm (s; CH$_3$); ^{19}F NMR (376 MHz, CDCl$_3$, 19 °C, CFCl$_3$): $\delta=-107.0$ (ddt, ^2J(F,F) = 89.8 Hz, ^3J(F,*cis*-F) = 31.9 Hz, ^4J(F,H) = 2.8 Hz, 1F; CF$_2$), -125.6 (ddt, ^3J(F,*trans*-F) = 114.1 Hz, ^2J(F,F) = 89.8 Hz, ^4J(F,H) = 4.1 Hz, 1F; CF$_2$), -174.1 ppm (ddt, ^3J(F,*trans*-F) = 114.1, ^3J(F,*cis*-F) = 31.9 Hz, ^3J(F,H) = 22.5 Hz, 1F; CF).

9: (*E*)-1,1,2-Trifluoro-5-phenylpenta-1,4-diene (procedure 4): The reaction mixture was dissolved in diethyl ether, filtered, extracted twice with brine and once with water (to remove DMF), and concentrated. ^{19}F NMR spectroscopy showed no unreacted tributyl(trifluoroethenyl)stannane. Vacuum distillation at 0 °C (0.3 Pa) yielded the product in 98 % purity according to ^{19}F NMR spectroscopy. ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C, TMS): $\delta=7.36$–7.17 (m, 5H; Ar-H), 6.53 (d, ^3J(H,H) = 15.8 Hz, 1H; Ph-CH), 6.13 (dt, ^3J(H,H) = 15.8, 6.7 Hz, 1H; CH), 3.12–3.22 ppm (m, 2H; CH$_2$); ^{13}C{^{1}H} NMR (100.4 MHz, CDCl$_3$, 22 °C, TMS): $\delta=153.2$ (td, ^1J(C,F) = 273 Hz, ^2J(C,F) = 46 Hz; CF$_2$), 136.6 (s; Ar-C1), 133.5 (s; Ph-CH), 128.6 (s; Ar-C3,C5), 127.7 (s; Ar-C4), 125.8–128.8 (m; CF), 126.3 (s; Ar-C2,C6), 121.9 (d, ^3J(C,F) = 13 Hz; CH), 29.3 ppm (dd, ^2J(C,F) = 22 Hz, ^3J(C,F) = 2.2 Hz; CH$_2$); ^{13}C{^{19}F} NMR (100.4 MHz, CDCl$_3$, 20 °C, TMS): $\delta=153.2$ (s; CF$_2$), 136.6 (s; Ar-C1), 133.5 (d, ^1J(C,H) = 152 Hz; Ph-CH), 128.6 (dd, ^1J(C,H) = 160 Hz, ^2J(C,H) = 7 Hz; Ar-C3,C5), 126.5–128.9 (m; Ar-C4), 127.3 (t, ^2J(C,H) = 8 Hz; CF), 126.0–127.4 (m; Ar-C2,C6), 121.9 (d, ^1J(C,H) = 206 Hz; CH), 29.3 ppm (t, ^1J(C,H) = 124 Hz; CH$_2$); ^{19}F NMR (376 MHz, CDCl$_3$, 20 °C, CFCl$_3$): $\delta=-105.5$ (ddt, ^2J(F,F) = 86.8 Hz, ^3J(F,F) = 32.6 Hz, ^4J(F,H) = 2.6 Hz; CF$_2$), -124.4 (ddt, ^2J(F,F) = 86.8 Hz, ^3J(F,F) = 114.5 Hz, ^4J(F,H) = 4.0 Hz; CF$_2$), -173.8 ppm (ddt, ^3J(F,F) = 114.5, 32.6 Hz, ^3J(F,H) = 21.8 Hz; CF); MS (70 eV, EI): m/z (%) = 198 (100) $[M]^+$, 183 (15), 177, 165, 151, 147, 133, 115, 102, 91, 78, 69, 55, 43.

10: 1,1,2-Trifluoro-4-phenylpenta-1,4-diene: 2-Phenyl-3-bromo-2-propene (**30**) was prepared by bromination of 2-phenylallyl alcohol with Br$_2$PPh$_3$.[63] This compound was coupled with stannane **21** (procedure 4) to yield **10**. The crude product was distilled at 0 °C (0.3 Pa) after aqueous workup. ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C, TMS): $\delta=7.60$–7.28 (m, 5H; Ar-H), 5.48 (s, 1H; =CH$_2$), 5.24 (s, 1H; =CH$_2$), 3.39–3.51 ppm (m, 2H; CH$_2$); ^{13}C{^{1}H} NMR (100.4 MHz, CDCl$_3$, 24 °C, TMS): $\delta=153.6$ (td, ^1J(C,F) = 274 Hz, ^2J(C,F) = 46 Hz; =CF$_2$), 140.4 (d, ^1J(C,F) = 173 Hz; =CF), 128.7 (s; Ar-C1), 128.5 (s; Ar-C3,C5), 128.0 (s; Ar-C4), 127.7 (d, ^3J(C,F) = 7.8 Hz; Ar), 125.9 (s; Ar-C2,C6), 115.4 (s; =CH$_2$), 32.0 ppm (dd, ^2J(C,F) = 22.4 Hz, ^3J(C,F) = 2.5 Hz; CH$_2$); ^{13}C{^{19}F} NMR (100.4 MHz, CDCl$_3$, 20 °C, TMS): $\delta=153.6$ (s; CF$_2$), 140.4 (s; CF), 128.5–128.9 (m; Ar-C1), 127.5–129.4 (m; Ar-C3,C5), 126.3–129.4 (m; Ar-C4), 125.1–126.7 (m; Ar-C2,C6), 115.4 (dt, ^1J(C,H) = 156 Hz, ^3J(C,H) = 5.1 Hz; =CH$_2$), 32.0 ppm (tdd, ^1J(C,H) = 129 Hz, ^3J(C,H) = 6.5 Hz, ^3J(C,H) = 11.4 Hz; CH$_2$); ^{19}F NMR (376 MHz, CDCl$_3$, 20 °C, CFCl$_3$): $\delta=-104.9$ (ddt, ^2J(F,F) = 84.7 Hz, ^3J(F,F) = 32.8 Hz, ^4J(F,H) = 2.5 Hz, 1F; =CF$_2$), -123.5 (ddt, ^2J(F,F) = 84.7 Hz, ^3J(F,F) = 114.5 Hz, ^4J(F,H) = 4.0 Hz, 1F; =CF$_2$), -173.0 ppm (ddt, ^3J(F,F) = 114.5, 32.8 Hz, ^3J(F,H) = 21.6 Hz, 1F; CF); MS (70 eV, EI): m/z (%) = 198 (100) $[M]^+$, 178 (12) $[M-\text{HF}]^+$, 147 (9) $[M-\text{CF}_2\text{H}]^+$, 103 (55) $[M-\text{C}_3\text{F}_3\text{H}_2]^+$, 95 (3) $[\text{C}_3\text{F}_3\text{H}_2]^+$, 77 (25) $[\text{C}_6\text{H}_5]^+$, 51 (12) $[\text{CF}_2\text{H}]^+$.

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Trifluoroethenylzinc chloride: 1,1,1,2-Tetrafluoroethane (12.8 g, 126 mmol) was condensed onto dry THF (500 mL) in a 1-L Schlenk flask equipped with a stirrer bar and cooled with liquid nitrogen. The mixture was warmed to −78 °C, and *n*-butyllithium (88 mL, 2.5 M solution in hexane, 220 mmol) was added dropwise. The solution was stirred at −78 °C for 1 h, and $ZnCl_2$ (15.0 g, 110 mmol in 150 mL dry THF) was added slowly to maintain the low temperature. The solution was stirred overnight while being warmed slowly to room temperature. The yield was about 75 % as determined by titration with hydrochloric acid. ^{19}F NMR (376 MHz, THF, 19 °C, $CFCl_3$): $\delta = -97.4$ (dd, ^3J(F,*cis*-F) = 33 Hz, ^2J(F,F) = 92 Hz, 1 F; CF_2), −130.4 (dd, ^2J(F,F) = 92 Hz, ^3J(F,*trans*-F) = 105 Hz, 1 F; CF_2), −194.4 ppm (dd, ^3J(F,*cis*-F) = 33 Hz, ^3J(F,*trans*-F) = 105 Hz, 1 F; CF). To crystallize the compound, a quantity of the solution was put into a Schlenk flask, most of the solvent was evaporated, and the residue was extracted with diethyl ether. The resulting solution was transferred to a Schlenk tube, and 1 equivalent of TMEDA (dried over calcium hydride) was added. The resulting complex immediately precipitated. The solvent was evaporated, and the precipitate was crystallized from THF. Slow cooling to −85 °C afforded large colorless single crystals of $[Zn(Cl)(C_2F_3)TMEDA]$, which were only soluble in THF. ^{19}F NMR (376 MHz, THF, 20 °C, $CFCl_3$): $\delta = -96.0$ (dd, ^3J(F,*cis*-F) = 34 Hz, ^2J(F,F) = 90 Hz, 1 F; CF_2), −129.0 (dd, ^2J(F,F) = 90 Hz, ^3J(F,*trans*-F) = 105 Hz, 1 F; CF_2), −193.0 ppm (dd, ^3J(F,*cis*-F) = 34 Hz, ^3J(F,*trans*-F) = 105 Hz, 1 F; CF).

Crystallography

Compound **2** was condensed in glass capillaries of 0.5-mm diameter and 0.01-mm wall thickness by using a glass vacuum line. A column of 3–4 mm of the liquid was cooled with liquid nitrogen, and the capillary was sealed under vacuum at a length of 30 mm. Upon warming to −78 °C in a dry ice/acetone bath, the capillary was mounted on an insulated arcless goniometer head while the sample was maintained at −78 °C to avoid destruction of the capillaries. The sample was mounted in the cold nitrogen-gas stream of an integrated cooling device onto a Bruker-AXS SMART1000 diffractometer. A single crystal was grown by cooling the sample well below melting point, with slow warming to determine the melting point and recooling to obtain a polycrystalline material. Setting of the temperature of the cold nitrogen-gas stream below but as close as possible (< 1 K) to the melting point resulted in a temperature gradient between the upper and lower part of the capillary, as the nitrogen-gas stream was not parallel to the capillary axis owing to the fixed χ angle of the diffractometer. Slow ϕ rotation resulted in single crystals after a few hours. The quality of the crystals and the progress of crystallization were checked by recording rotational frames and matrix runs. The crystals were cooled slowly to the temperature given in Table 6. A single crystal of $[Zn(Cl(C_2F_3)TMEDA]$ was grown by slowly cooling a solution in THF to −84 °C. A few crystals were transferred by pipette onto filter paper, which was mounted in a stream of cold nitrogen onto an apparatus as described in the literature.[64] A suitable crystal was selected by using a microscope, mounted onto a glass fiber with silicone grease, and transferred into the cold gas stream of a diffractometer without interruption of the cooling.

Crystal data and details of the structure determinations are presented in Table 6. Intensity data were collected on a Bruker AXS Smart diffractometer. Structures were solved by direct methods (SHELXS-97).[65] Details of the data collection and structure refinement are summarized in Table 6. The hydrogen atom of pentafluorobutadiene was found in the difference Fourier map and refined isotropically. The hydrogen atoms of $[Zn(Cl)(C_2F_3)TMEDA]$ were refined in calculated positions by using isotropic thermal parameters (1.2 and 1.5 U_{eq} (C) for methyl). Anisotropic thermal parameters were applied to all non-hydrogen atoms. Refinement for all structures on F^2 were achieved with the SHELXL-97 system.[65] Drawings of the molecules were made with ORTEP for Windows.[44] CCDC-661005 ($[Zn(Cl)(C_2F_3)TMEDA]$), -661004 (**2**), -661007 (**18**), and -661006 ($P(O)Cy_2R$) contain the supplementary crystallographic data (excluding structure factors) for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk) or at www.ccdc.cam.ac.uk/data_request/cif.

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