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Regioselective Coupling of Pentafluorophenyl Substituted Alkynes: Mechanistic Insight into the Zirconocene Coupling of Alkynes and a Facile Route to Conjugated Polymers Bearing Electron-Withdrawing Pentafluorophenyl Substituents

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Abstract: The reaction of Cp_2ZrCl_2 with 2 equiv of BuLi at −78 °C, followed by the addition of an unsymmetrical tetra- or pentafluorophenyl substituted alkyne $R^1C{\equiv}CAr_f$ (R^1, Ar_f = $(CH_2)_4Me$, $p{-}C_6F_4H$; Me, $p{-}C_6F_4H$; Ph, C_6F_5), resulted in regioselective couplings of these alkynes to zirconacyclopentadienes in which the Ar_f substituents preferentially adopt the 3,4-positions (**$\beta\beta$**) of the zirconacyclopentadiene ring. With $Cp_2Zr(py)(Me_3SiC{\equiv}CSiMe_3)$ as the zirconocene reagent, the couplings could be carried out at room temperature; however, at higher temperatures significant quantities of the 2,4-fluoroaryl substituted ($\alpha\beta$) isomers were also formed. None of the conditions employed produced the 2,5-fluoroaryl substituted ($\alpha\alpha$) isomers. These fluoroaryl-substituted zirconacyclopentadienes were readily converted to butadienes via reactions with acids. The zirconacyclopentadiene Cp_2ZrC_4-2,5-Ph_2-3,4-$(C_6F_5)_2$, which resulted from the coupling of $PhC{\equiv}C(C_6F_5)$, was converted to the corresponding thiophene by reaction with S_2Cl_2, and to an arene by reaction with $MeO_2CC{\equiv}CCO_2Me$/CuCl. Mechanistic studies on zirconocene couplings of (p-$CF_3C_6H_4$)$C{\equiv}C$(p-MeC_6H_4) indicate that the observed regioselectivities are determined by an electronic factor that controls the orientation of at least one of the two alkynes as they are coupled. Additionally, these studies suggest an unsymmetrical transition state for the zirconocene coupling of alkynes, and this is supported by DFT calculations. The reaction of $[(C_6F_5)C{\equiv}CCH_2]_2CH_2$ with $Cp_2Zr(py)(Me_3SiC{\equiv}CSiMe_3)$ resulted in a zirconacyclopentadiene in which the pentafluorophenyl substituents have been forced into the 2,5-positions ($\alpha\alpha$). Zirconocene coupling of the diyne $(C_6F_5)C{\equiv}C$-1,4-$C_6H_4{-}C{\equiv}C(C_6F_5)$ provided a route to conjugated polymers bearing electron-withdrawing pentafluorophenyl groups.

Introduction

Conjugated oligomers and polymers have attracted interest for their ability to replace inorganic components in electronic devices such as light-emitting diodes (LEDs)[1,2] and thin-film transistors.[3] The majority of materials used in these electronic devices are good positive charge (p-type) semiconductors, such as polythiophene,[4] poly-*p*-phenylene, and poly-*p*-phenylvinylene.[5] In general, these polymers possess relatively high energy LUMOs, which results in poor negative charge (n-type) conduction and limits their utility in electronic devices.[6] The development of n-type organic semiconductors could result in improved efficiencies for LEDs[7] and new applications for organic semiconductors.

A strategy for obtaining materials with improved electron-transport properties is the replacement of hydrogen by fluorine in the monomer units.[8−14] The electronegative fluorine substituents lower the energy of the LUMOs in these polymers and provide increased kinetic stability by virtue of the strength of the C−F bonds and the steric protection offered by the larger radius of fluorine vs hydrogen.[15] Often, the syntheses of these polymers are neither facile nor high yielding. Furthermore, despite the current interest in fluorinated polymers, few

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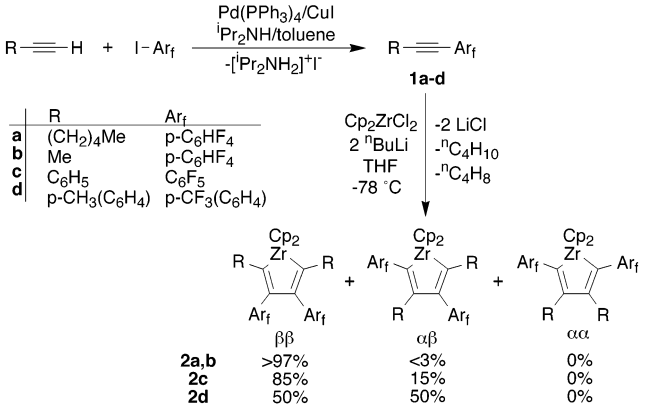
conjugated materials have been prepared that contain the considerably more electron-withdrawing perfluorophenyl group as a substituent,[16,17] and simple methodologies for the preparation of perfluoroaryl-substituted conjugated polymers and oligomers are not well developed.

Our studies have focused on the use of zirconocene synthons for the coupling of alkynes to produce zirconacyclopentadiene-containing macrocycles,[18−24] oligomers[25,26] and polymers.[27−29] The zirconacyclopentadiene moiety can then be converted into other derivatives such as dienes,[30] arenes,[31−36] cyclopentadienes[37,38] and heterocycles[39] such as thiophenes,[40,41] siloles,[42,43] phospholes,[44] germoles,[27] pyrroles,[45] and thiophene oxides.[26] The formation of macrocycles by the zirconocene coupling of alkynes requires a substituted diyne that couples in a regioselective manner, and reversible diyne coupling reactions. To date, the only alkyne substituent that has fulfilled these roles are silyl groups, which couple exclusively into the 2,5 ($\alpha\alpha$) positions of the zirconacyclopentadiene ring.[46−48] Both the selectivity and the reversibility of the coupling of silyl substituted alkynes may be due to the size of these groups; however, little is known about the role of electronic effects in the coupling of alkynes by the zirconocene fragment.[49] The availability of additional substituents which could direct regioselective alkyne coupling would increase the scope of this reaction for the synthesis of functionalized conjugated polymers and macrocycles.

Scheme 1



	R	Ar$_f$
a	$(CH_2)_4Me$	p-C_6HF_4
b	Me	p-C_6HF_4
c	C_6H_5	C_6F_5
d	p-$CH_3(C_6H_4)$	p-$CF_3(C_6H_4)$

This paper describes the effects of electron-withdrawing perfluoroaryl groups on the zirconocene coupling of alkynes, and demonstrates that these substituents direct the regiochemistry of the coupling such that the perfluoroaryl groups selectively adopt the 3,4-positions ($\beta\beta$) of the zirconacyclopentadiene ring. A study of the mechanism of this reaction indicates that the coupling of alkynes by the zirconocene fragment occurs via an unsymmetrical transition state. Preliminary investigations indicate that this β-directing effect may be used to generate pentafluorophenyl-substituted conjugated polymers, which may have applications as electron-transport materials.

Results and Discussion

Regiochemistry of the Zirconocene Coupling of Fluorophenyl-Substituted Alkynes. The fluorophenyl-substituted alkynes used in this study (**1a**−**d**) were synthesized in moderate to high yields by the Pd(PPh$_3$)$_4$/CuI-catalyzed coupling of the appropriate fluoroaryl iodide with a terminal alkyne. Reaction of alkynes **1a**−**c** with Negishi's zirconocene synthon[50] at low temperature followed by warming to room temperature over 6 h afforded zirconacyclopentadienes **2a**−**c** in high yields, as shown in Scheme 1. For **1a** and **1b**, one of the three possible zirconacyclopentadiene isomers was formed almost exclusively (>97%); however, the phenyl-substituted alkyne **1c** produced the symmetrical isomer **2c**($\beta\beta$) in 85% yield and the unsymmetrical coupling product **2c**($\alpha\beta$) in 15% yield. The selectivities of these reactions were determined by ^{1}H, ^{13}C{^{1}H} and ^{19}F{^{1}H} NMR spectroscopies of the crude reaction products.

To determine the connectivity in **2a**−**b** the corresponding hydrolyzed compounds **3a** and **3b** were synthesized as shown in Scheme 2. The ^{1}H NMR spectra of **3a**,**b** contain triplet and quartet peaks at δ 5.56 ($^3J_{HH}$ = 7.2 Hz) and 5.42 ($^3J_{HH}$ = 6.8 Hz) for the vinyl protons coupled to the methylene and methyl groups, respectively, which indicates that the tetrafluorophenyl groups are in the 3,4-positions of the precursor zirconacyclopentadienes. In the case of **2c**($\beta\beta$), which was isolated by crystallization from diethyl ether, X-ray crystallography conclusively established the molecular structure (Figure 1). This compound crystallizes with one equiv of ether. Due to disorder

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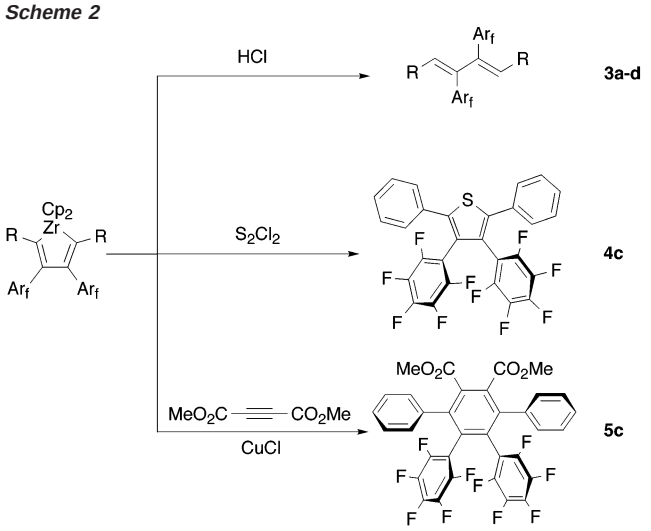
Scheme 2



in the cocrystallized solvent and Cp rings, only the zirconium and the fluorine atoms were modeled anisotropically.

The selectivity of the alkyne coupling reaction was found to depend somewhat on the reaction conditions. When the reaction mixtures of either **1a** or **1b** with Negishi's zirconocene synthon in THF were warmed quickly from −78 °C, up to 12% of the $\alpha\beta$ products were formed, as determined by integration of the vinylic protons in the ^{1}H NMR spectra of the hydrolyzed samples. When $Cp_2Zr(py)(Me_3SiC{\equiv}CSiMe_3)$[23,51] was used as the zirconocene synthon in toluene at 90 °C, up to 30% of the $\alpha\beta$ isomer was formed, but no detectable amount of the $\alpha\alpha$ isomer was ever observed. As noted earlier, the coupling of the phenyl-substituted alkyne **1c** was slightly less selective than those of the alkyl-substituted alkynes (Scheme 1). It is also notable that the reaction of alkyne **1c** with $Cp_2Zr(py)(Me_3SiC{\equiv}CSiMe_3)$ is slow at room temperature, whereas alkynes **1a** and **1b** react within seconds.

The selectivity found in the coupling of the fluoroaryl/alkyl-substituted alkynes is very different from that found for nonfluorinated aryl/alkyl-substituted alkynes. For example, $PhC{\equiv}C(CH_2)_4CH_3$ reacts with Negishi's zirconocene synthon to produce a coupling product with both phenyl groups in the α position (15%) and the $\alpha\beta$ coupled product (85%), but none of the product with $\beta\beta$ phenyl substitution.[29] The selectivities observed for the couplings of pentafluorophenyl-substituted alkynes are also different from those observed in $CpCo(CO)_2$-mediated alkyne couplings.[52,53]

Zirconocene Coupling Routes to Fluorinated Derivatives. Besides hydrolysis, two other transformations of zirconacycle **2c($\beta\beta$)** were carried out. The reaction of **2c($\beta\beta$)** with S_2Cl_2 and dimethyl acetylenedicarboxylate gave thiophene **4c** and arene **5c**, respectively, in high yields (Scheme 2).[32,41] Single crystals of **4c** suitable for X-ray analysis were grown from an acetonitrile/cyclohexane solution. Its structure is shown in Figure 2. The UV−vis spectrum of **4c** exhibited a λ_{max} value of 320 nm, which is slightly blue-shifted relative to that for 2,5-diphenyl-3,4-propanediyl-thiophene (330 nm).[25] This may be due to a smaller degree of conjugation for **4c**, which may result from a larger deviation from planarity due to the larger size of the pentafluorophenyl substituents compared to the 3,4-propanediyl group. This hypothesis is supported by the solid-state molecular structure of **4c** which exhibits rings that are not coplanar.

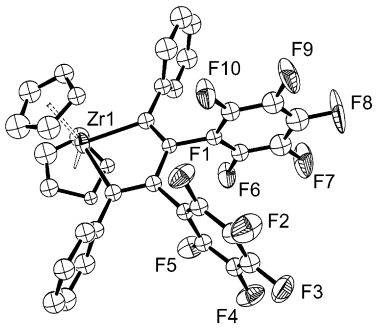


Figure 1. ORTEP depiction of the solid-state molecular structure of **2c($\beta\beta$)**. Hydrogen atoms and the cocrystallized ether molecule are omitted for clarity. Ellipsoids are drawn with 50% probabilites. Only Zr(1) and F(1)−F(10) were refined anisotropically. Selected bond lengths(Å), bond angles(°): Zr1−C11, 2.281(7); Zr1−C14, 2.278(6); C11−C12, 1.355(8); C12−C13, 1.488(8); C13−C14, 1.333(9); Zr1−C11−C15, 129.5(5); Zr1−C14−C33, 130.0(5).

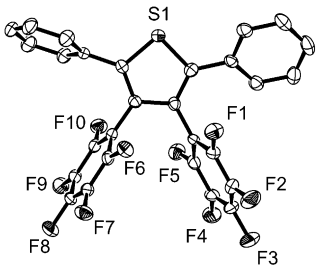


Figure 2. ORTEP diagram of one of the crystallographically independent molecules of thiophene **4c**. Hydrogen atoms and the cocrystallized cyclohexane molecule are omitted for clarity. Thermal ellipsoids are drawn with 50% probabilities.

Mechanistic Study. To determine the relative importance of electronic and steric effects in the regioselective coupling of fluoroarylalkynes, the zirconocene coupling of *p*-tolyl-*p*-(trifluoromethylphenyl)ethyne (**1d**) was examined. With the electron-withdrawing group in the distal para position, the influence of steric effects during the formation of the zirconacycle should be minimized. The coupling reactions were carried out by using either Negishi's zirconocene synthon at low temperature or $Cp_2Zr(py)(Me_3SiC{\equiv}CSiMe_3)$ at room temperature. In the absence of either electronic or steric effects, a 1:2:1 ratio ($\alpha\alpha$:$\alpha\beta$:$\beta\beta$) for the three possible isomers would be expected. In fact, the ^{1}H and ^{19}F{^{1}H} NMR spectra indicate that the $\beta\beta$ isomer and the unsymmetrical $\alpha\beta$ isomer were formed as the major products in a 1:1 ratio. This product distribution was not strongly affected by reaction conditions; however, the room-temperature coupling using $Cp_2Zr(py)(Me_3SiC{\equiv}CSiMe_3)$ produced a small amount of the $\alpha\alpha$ isomer, which accounted for 5% of the coupling product (5% $\alpha\alpha$, 45% $\alpha\beta$, 50% $\beta\beta$). The two major products could not be separated to conclusively identify the symmetrical complex as the $\beta\beta$ isomer, so further reactions were carried out to ascertain this unequivocally. Hydrolysis of a 1:1 mixture of the symmetrical and unsymmetrical zirconacycles (**2d($\beta\beta$)** and **2d($\alpha\beta$)**) gave a mixture of two dienes (**3d($\beta\beta$)** and **3d($\alpha\beta$)**), which was partially separated by column chromatography. The 2D C−H correlation NMR spectra (HMQC, optimized for short- and long-range coupling) and 2D ^{1}H−NOESY NMR-experiments of the symmetrical

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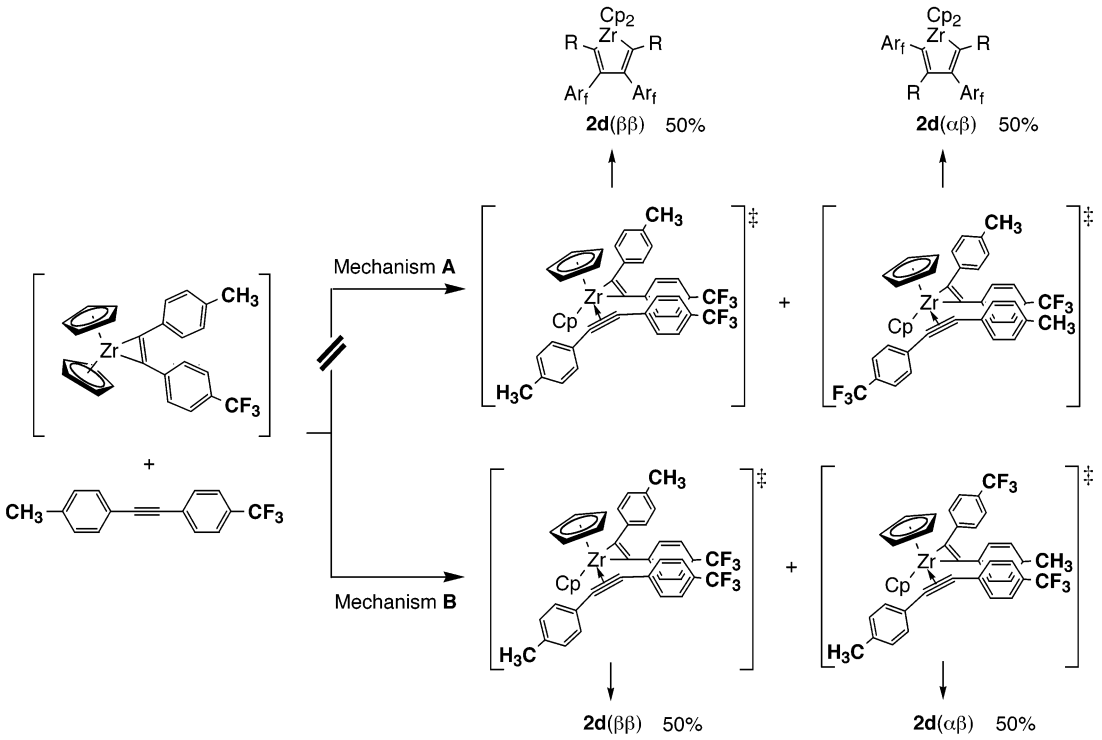
Scheme 3



compound confirmed that it is the $\beta\beta$ isomer (see the Supporting Information). The preferential formation of the $\beta\beta$ and $\alpha\beta$ isomers provides clear evidence that there is a strong electronic effect in the selectivity of the zirconocene alkyne coupling reaction.

These results also indicate that a stepwise mechanism is operative. It is believed[54] that the initial reaction steps of zirconocene alkyne coupling involve the formation of a transient 16-electron alkyne complex,[55] such as the one shown on the left side of Scheme 3. This transient zirconacyclopropene then rapidly inserts a second equiv of alkyne **1d** to form the observed zirconacyclopentadiene products (**2d(**$\beta\beta$**)** and **2d(**$\alpha\beta$**)**). The presence of only two isomers in the product mixture (**2d(**$\beta\beta$**)** and **2d(**$\alpha\beta$**)**) implies that the transition state of the C−C bond-forming step does not contain two equally activated, metal-bound alkynes, as is often assumed in the coupling of alkynes by zirconocene.[56−58] One possible explanation for the observed product distribution is that in the unobserved intermediate monoalkyne complex $Cp_2Zr[(MeC_6H_4)CC(C_6H_4CF_3)]$, the Zr−C bond associated with the more electron-withdrawing *p*-trifluoromethylphenyl substituent is significantly more reactive toward the insertion of a second equiv of alkyne. This reaction pathway is labeled mechanism **A** in Scheme 3. A second possible explanation for the selectivity in the coupling of alkyne **1d** involves comparable reactivity for the two Zr−C bonds of the intermediate zirconacyclopropene complex, $Cp_2Zr[(MeC_6H_4)CC(C_6H_4CF_3)]$, toward insertion, but regioselectivity in the orientation of the second equiv of alkyne as it inserts. For example, in this case the incoming alkyne orients itself such that the more electron-withdrawing *p*-trifluoromethylphenyl group occupies the β-position in the zirconacyclopentadiene product (mechanism **B** in Scheme 3). These mechanisms only differ in the transition states by which the $\alpha\beta$ isomer forms. It should be noted that these are limiting cases, and it is possible that with some alkynes both effects could operate to some extent.

By determining the regiochemistries of reactions of fluoroaryl-substituted alkynes with a variety of zirconacyclopropene complexes, it should be possible to distinguish between mechanisms **A** and **B**. However, zirconacyclopropene complexes of the type $Cp_2Zr(RC{\equiv}CR')$ have rarely been observed and in general are not isolable.[59] An alternative approach involves the transient generation of such a species, which may then be trapped by an added fluoroaryl-substituted alkyne. The microscopic reverse of alkyne coupling by zirconocene (the elimination of an alkyne from a zirconacyclopentadiene) is presumed to generate a zirconacyclopropene intermediate,[60] but this reaction has been observed only in the case of zirconacyclopentadienes bearing bulky substituents in the α positions, such as trimethylsilyl or *tert*-butyl.[49,56,60] However, to further probe the regioselectivity observed in the coupling of **1d** we sought to observe evidence for reversibility in other zirconacyclopentadienes using relatively high reaction temperatures.

Heating a solution of the tetraphenyl-substituted zirconacyclopentadiene $Cp_2ZrC_4Ph_4$ at 150 °C in the presence of an excess (10 equiv) of **1d** allowed observation of new zirconacyclopentadiene products (by ^1H and $^{19}F\{^1H\}$ NMR spectroscopy), and PhC≡CPh was liberated (Scheme 4). This reaction was very slow at this temperature, taking over 24 h to go to completion. After 1 h of heating two new products were observed and less than 5% of the $Cp_2ZrC_4Ph_4$ had been

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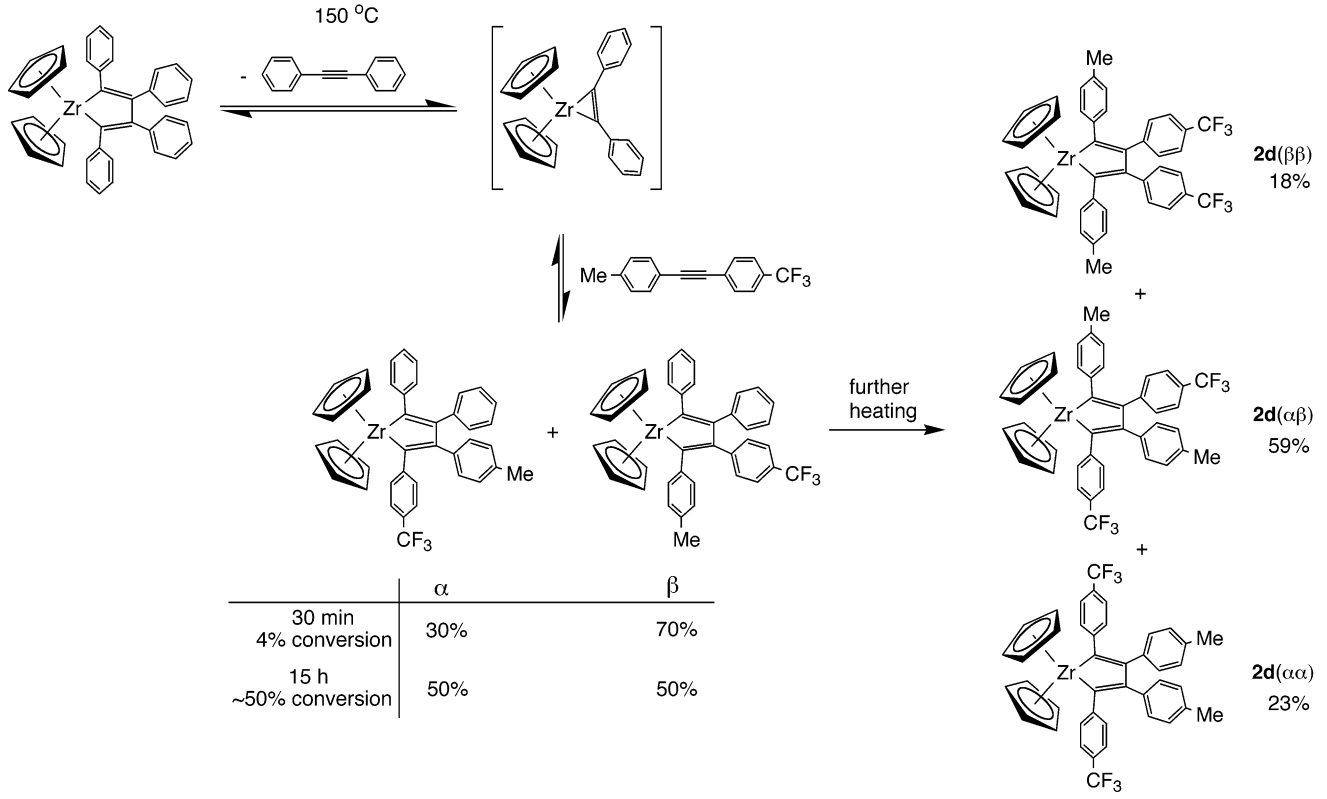
Scheme 4



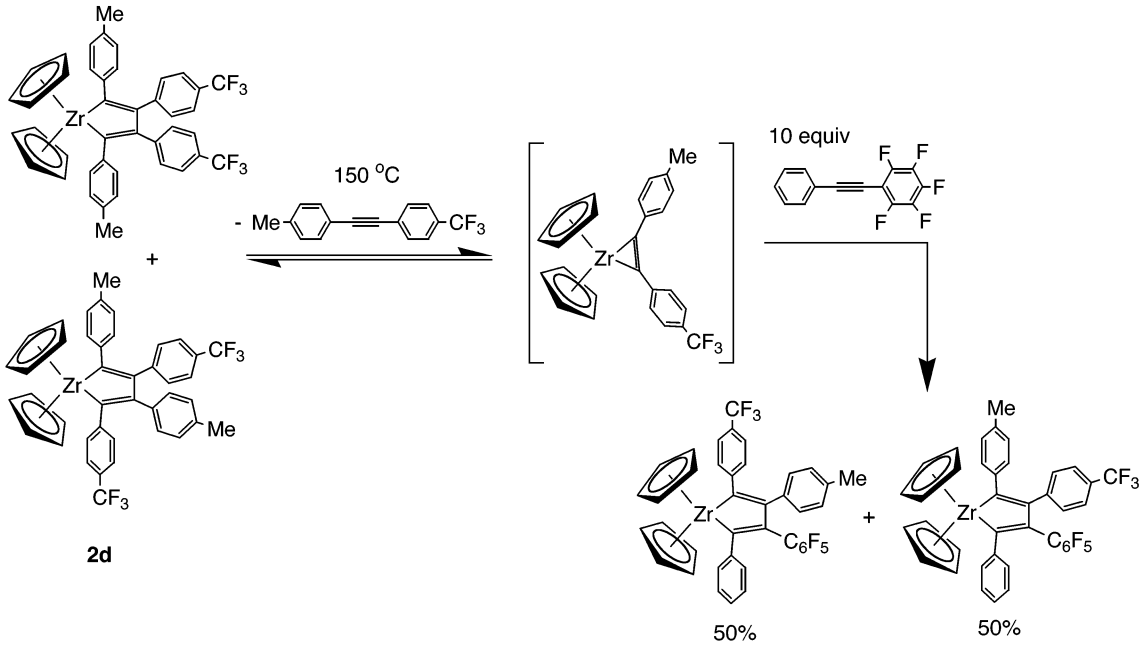
	α	β
30 min 4% conversion	30%	70%
15 h ~50% conversion	50%	50%

consumed. These products each exhibit a single resonance in the $^{19}F\{^1H\}$ NMR spectrum, one with a chemical shift (δ 0.77) similar to that of **2d(*ββ*)** and one with a chemical shift (δ 1.22) that is similar to one of the resonances of **2d(*αβ*)**. On the basis of such comparisons, these two species appear to be the products of mixed coupling between diphenylethyne and **1d** (Scheme 4, where the *β* isomer has the *p*-trifluoromethylphenyl substituent in the 3-position of the zirconacyclopentadiene and the α-isomer contains the *p*-trifluoromethylphenyl substituent in the 2-position). The initial ratio of products (70% *β* isomer) appears to be kinetically determined, because continued heating eventually generates a thermodynamic product mixture of these two monosubstituted isomers, in which the α and the *β* isomers are present in approximately a 1:1 ratio. Also observed in the product mixture are the disubstituted products **2d(*ββ*)** and **2d(*αβ*)**. Further heating over a total of 72 h provides a product mixture containing the isomers **2d(*αβ*)**, **2d(*ββ*)**, and **2d(αα)**; the thermodynamic product distribution of disubstituted products is 23% αα: 59% *αβ*: 18% *ββ*, as measured from both ^1H and $^{19}F\{^1H\}$ NMR spectroscopy. This is close to the 25:50:25 statistical product distribution expected in the absence of any regioselectivity; however, it is notable that the αα product, which is kinetically disfavored, is actually thermodynamically slightly favored over the *ββ* isomer. The observation of some selectivity in the initial formation of the monosubstituted α and *β* isomers in this reaction indicates that mechanism **A** is a poor description of the reaction mechanism, because it predicts that the second alkyne inserts with no selectivity. In contrast, some selectivity is observed even at elevated temperatures. This argument assumes that a dissociative mechanism is operating (vide infra).

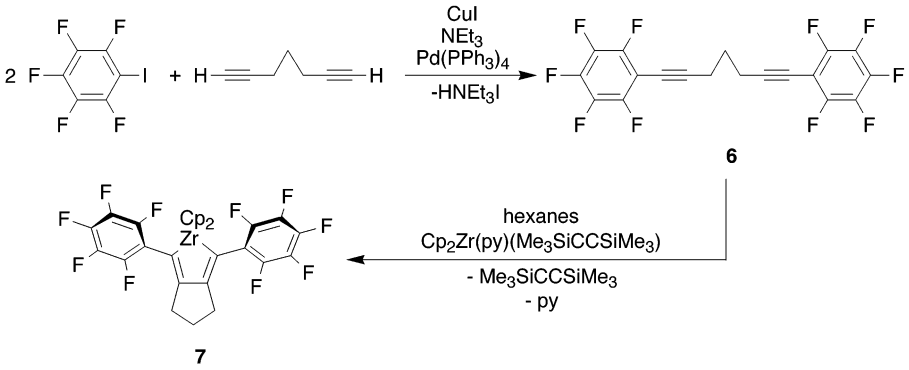
A second way to distinguish between the limiting mechanisms **A** and **B** of Scheme 3 involves heating a mixture of **2d(*ββ*)** and **2d(*αβ*)** in the presence of an excess of an alkyne, to displace 1 equiv of (*p*-$CF_3C_6H_4$)C≡C(*p*-$CH_3C_6H_4$) and form a new zirconacyclopentadiene. Mechanism **A** predicts that the single, transient zirconacyclopropene generated by heating a mixture of **2d(*αβ*)** and **2d(*ββ*)** should produce zirconacyclopentadienes in which the *p*-$CF_3C_6H_4$ group is in the *β* position, whereas mechanism **B** predicts that the *p*-$CF_3C_6H_4$ group should be equally distributed between the α and *β* positions of the product. Heating a benzene-d_6 solution of **2d(*ββ*)** and **2d(*αβ*)** at 140 °C in the presence of an excess of PhC≡C(C_6F_5) for 2 h produced a 1:1 ratio of two new monosubstituted products, as shown in Scheme 5, along with unreacted **2d(*ββ*)** and **2d(*αβ*)**. The ^1H and $^{19}F\{^1H\}$ NMR spectra of the reaction solution indicate the formation of two products which exhibit chemical shifts for their *p*-CF_3 groups (δ 0.92, 0.42) that are consistent with those previously observed for α-$C_6H_4CF_3$ and *β*-$C_6H_4CF_3$ isomers, respectively. Resonances for the two C_6F_5 groups are nearly overlapping, indicating that these substituents occupy the *β* positions in both isomers. These results provide further support that mechanism **B** is operative in the formation of **2d(*ββ*)** and **2d(*αβ*)**, and that the strongest electronic effect is exhibited by the inserting alkyne. Continued heating of the reaction mixture for 24 h produces a thermodynamic product mixture of the monosubstituted isomers, in which one isomer is slightly favored (58% α-$C_6H_4CF_3$: 42% *β*-$C_6H_4CF_3$), and also results in the formation of the disubstituted products **2c(*ββ*)** and **2c(*αβ*)**, as expected. Experiments performed with varying amounts of excess alkyne revealed no significant difference in reaction rates, which confirms that this reaction occurs by a dissociative mechanism, rather than by an associative mechanism.

The absence of αα isomers in the coupling of **1a**−**c** can therefore be rationalized by mechanism **B** in Scheme 3. However, in the case of the pentafluorophenyl-substituted

Scheme 5



Scheme 6



alkynes, an additional effect must be operating, because the $\beta\beta$ coupling product is kinetically favored over the $\alpha\beta$ product. This could be an electronic effect that is not observed with the *p*-trifluoromethylphenyl group because it is less electron withdrawing than the pentafluorophenyl substituent; however, it is possible that the steric bulk of the pentafluorophenyl group is also important in the observed regioselectivity.[61−64] Further mechanistic information could be obtained from reversible coupling experiments with **2c($\beta\beta$)**; however, heating this zirconacyclopentadiene at 150 °C provided no evidence that this coupling was reversible, either via alkyne exchange reactions or by the formation of **2c($\alpha\beta$)**. It was therefore also impossible to determine the thermodynamic product mixture for the coupling of **1c**, or to determine if the $\alpha\alpha$ isomer is a viable thermodynamic product despite being kinetically disfavored (as was observed in the coupling of **1d**).

To determine if it is possible to overcome the regioselective effect of the pentafluorophenyl group using a linking group, the bis(pentafluorophenyl)-substituted 1,6-heptadiyne (**6**) was subjected to coupling conditions with the zirconocene synthon $Cp_2Zr(py)(Me_3SiC{\equiv}CSiMe_3)$. This resulted in formation of zirconacyclopentadiene **7**, as shown in Scheme 6. Crystals of **7** suitable for X-ray diffraction were obtained by slow evaporation of a toluene solution. The solid-state molecular structure (Figure 3) clearly demonstrates that it is possible to couple alkynes with pentafluorophenyl groups in the two α positions of the zirconacyclopentadiene. The structure has noncrystallographic pseudo-mirror symmetry, such that the mirror plane lies perpendicular to the zirconacyclopentadiene ring. The pentafluorophenyl rings form angles of 67.2° and 64.8° to the mean plane of the four carbon atoms of the zirconacyclopentadiene. The pentafluorophenyl ring ipso-carbons C18 and C24 lie out of the mean plane of the zirconacyclopentadiene by 0.29 and 0.22 Å, respectively. This distortion may be due to steric interactions between the pentafluorophenyl rings and the cyclopentadienyl ligands; however, other aspects of the structure, such as the Zr1−C17 and Zr1−C11 distances of 2.245(4) and 2.241(4) Å, respectively, are not significantly different from comparable parameters in other zirconacyclopentadienes.

DFT Calculations. The coupling of alkynes by zirconium has been assumed to occur via an intermediate or transition state in which the two alkynes are activated to an equal extent by

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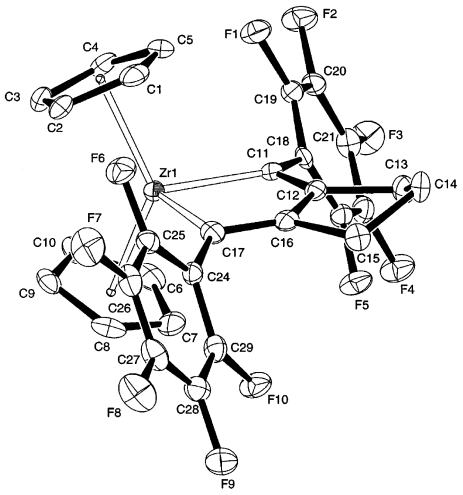

Figure 3. ORTEP depiction of the solid-state molecular structure of **7**. Hydrogen atoms and the cocrystallized toluene molecule are omitted for clarity. Selected bond lengths(Å), bond angles(°) and dihedral angles(°): Zr1−C11, 2.245(4); Zr1−C17, 2.241(4); C11−C12, 1.341(6); C12−C16, 1.516(5); C16−C17, 1.347(5); C17−C24, 1.484; C11−C18, 1.481(6); Zr1−C11−C18, 135.3(3); Zr1−C17−C24, 138.4(3); Cp(centroid)-Zr−Cp(centroid), 131.74(2), C12−C16−C17−C24, 170.4(4); C16−C12−C11−C18, −167.0(4), C16−C17−C24−C25, 120.2(4); C12−C11−C18−C19, −125.6(4).

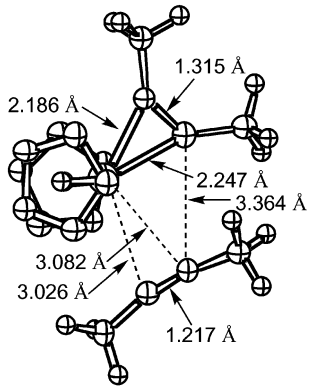

Figure 4. Calculated transition state for the coupling of MeC≡CMe by Cp_2Zr with selected bond lengths and interatomic distances. Cyclopentadienyl hydrogen atoms are omitted for clarity.

the metal center prior to zirconacyclopentadiene formation;[56] however, the mechanistic studies utilizing alkyne **1d** indicate that this is not true. To provide further evidence that an unsymmetrical transition state is relevant in the coupling of alkynes by zirconocene, DFT calculations were performed on the $C_\beta-C_\beta$ bond cleavages of $Cp_2ZrC_4Me_4$ and **2c(*ββ*)** using the B3/LYP level of theory and the LACVP* basis set. A transition state for $C_\beta-C_\beta$ bond cleavage was found by optimizing the ground state of the zirconacyclopentadiene, and then performing a coordinate search in which the $C_\beta-C_\beta$ bond was constrained to longer lengths in small increments, with the structure being optimized with this single constraint at each point. From these data we determined that the transition state occurred near a $C_\beta-C_\beta$ separation of 3.3 Å. A QST (quadratic synchronous transit)-guided search then located a transition state very similar to that found using the coordinate search. This transition state is shown in Figure 4. The calculated transition state for the coupling of two alkynes by the zirconocene fragment contains one alkyne that is strongly activated with normal Zr−C bond lengths, whereas the second alkyne is only weakly interacting with the zirconium center. The other optimized structures demonstrate that the subsequent formation of the $C_\beta-C_\beta$ bond occurs via a bis-alkyne complex in which both alkynes are equally activated by the zirconium center; however, this bis-alkyne complex is neither an intermediate nor a transition state on the reaction pathway. The weakly bound alkyne in the calculated transition state has a C≡C bond distance of 1.217 Å, and is not strongly activated. Conversely, the strongly bound alkyne has a C−C distance of 1.315 Å, which is the appropriate distance for a double bond. The near linearity of the weakly bound alkyne is also evidence of the negligible back-bonding from the zirconium to this moiety in the calculated transition state. It is notable that for both alkyne ligands in the transition state, the Zr−C distance to the carbons on the outside of the Cp_2Zr wedge (C_α in the product) are shorter than the adjacent Zr−C_β distances by ∼0.06 Å.

A similar approach was taken in modeling the coupling of PhC≡C(C_6F_5) by Cp_2Zr. Starting from the optimized ground-state structure of the zirconacyclopentadiene **2c(*ββ*)**, a coordinate search was performed with the $C_\beta-C_\beta$ bond length being increased in small increments, and single constraint geometry optimizations were performed at each point. The approximate transition state structure for alkyne coupling, determined in this manner, is shown in Figure 5. This transition state is qualitatively similar to that shown in Figure 4 for the coupling of MeC≡CMe, in that one alkyne is coordinated to the metal and strongly activated while the second alkyne is in the process of coordinating to the metal center. The differences between the two Zr−C bond lengths for each alkyne moiety are even larger in this transition state than those shown in Figure 4. However, this may be the result of a somewhat later transition state for $C_\beta-C_\beta$ formation in this case.

The coupling of alkyne **1d** by zirconocene discussed in the previous section demonstrated the importance of an electronic effect in the regioselectivity of this reaction. Interestingly, this effect appears to be exerted mainly by the second alkyne, which is not strongly bound to zirconium in the transition state. A possible interpretation of this effect is based on a preferred electrostatic interaction between the zirconium center and the more electron-rich carbon of the C≡C unit (the one bearing the *p*-$CH_3C_6H_4$ group). Alternatively, it may be that increased molecular orbital overlap between a filled, zirconium-based a_1 orbital occurs with the LUMO of the alkyne via direct interaction with the carbon bound to the *p*-$CH_3C_6H_4$ group (where the LUMO has a stronger contribution).

In the coupling of fluoroaryl-substituted alkynes **1a**−**1c** both the strongly and weakly bound alkynes in the proposed transition state appear to affect the regioselectivities, as suggested by the very high ratio of *ββ*/*αβ* isomers (Scheme 1). In these cases, the insertion into the zirconacyclopropene intermediate preferentially occurs into the Zr−C bond associated with the perfluoroaryl group. One explanation for the additional selectivity observed with pentafluorophenyl substituents is based on the frontier orbital interactions between the Cp_2Zr fragment and the alkyne moieties. The overlap between the zirconium-based orbital of a_1 symmetry and the π^* LUMO of the alkyne moiety should be greater in the *ββ* transition state than the *αβ* transition state (Figure 5), because the contribution to the π^* LUMO is larger on the side of the alkyne which bears the less electron-withdrawing substituent. A similar argument could be made for

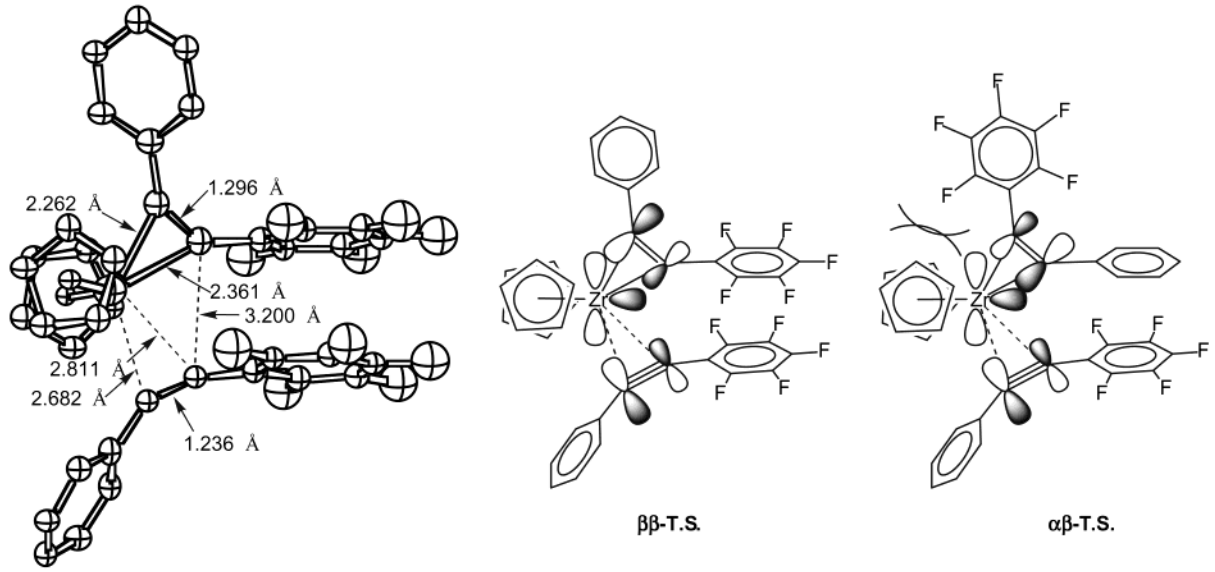

Figure 5. Calculated transition state of the coupling of PhC≡C(C_6F_5) by Cp_2Zr with selected bond lengths and depictions of selected orbital overlaps and steric interactions in the postulated transition states for the formation of **2c(*ββ*)** and **2c(α*β*)**. All hydrogen atoms are omitted for clarity.

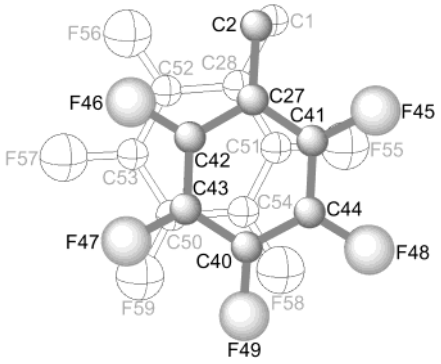

Figure 6. View of the stacking of the pentafluorophenyl rings in the calculated transition state for the coupling of PhC≡C(C_6F_5) by Cp_2Zr. Selected distances (Å) under 3.4 Å: F47−C50, 3.267; F46−F52, 3.267; F55−C41, 3.172; F55−C44, 3.325; F58−C40, 3.369; F49−F58, 3.346; C27−C28, 3.283; C54−C40, 3.379; C54−C43, 3.393; C42−C28, 3.332.

the orientation of the second weakly bound alkyne moiety. The difference in Zr−C bond lengths to the two adjacent carbons of each alkyne could also play an important role in orbital overlap; both central Zr−C bond lengths in the transition state are longer than the adjacent Zr−C bond lengths for both alkynes. Also, a steric effect could be important here, because the movement of the bound alkyne across the Cp_2Zr wedge will increase the steric interactions between the cyclopentadienyl ligands and the ortho fluorine atoms of the fluorinated aryl groups.[61−64] These orbital overlaps and steric interactions for the transition states which lead to **2c(*ββ*)** and **2c(α*β*)** are depicted in Figure 5.

An additional feature of the calculated transition state for PhC≡C(C_6F_5)-coupling is the near parallel arrangement of the pentafluorophenyl rings (Figure 5). In this modeled transition state, there are many short contacts between the carbon atoms and fluorine atoms of these two aromatic rings. This is illustrated from a different viewpoint in Figure 6, which also provides interatomic distances that are less than 3.4 Å. These distances are comparable to those observed in structures with attractive $\pi-\pi$ interactions;[65−67] however, the exact stacking of the rings is distorted compared to other commonly observed $\pi-\pi$ interactions. This is probably due to the geometrical requirements of alkyne binding to the transition metal. Although it is difficult to determine the importance of this $\pi-\pi$ interaction, it provides an alternative explanation for the β-directing effect of the pentafluorophenyl group. In fact, the small energy difference between the transition states that lead to the $\beta\beta$ and $\alpha\beta$ coupled products for **1a**−**c** makes it difficult to ascertain what the most important effect is in the regioselectivity of this coupling reaction.

Zirconocene Coupling Routes to Fluorinated Polymers. Preliminary investigations indicate that the regioselective zirconocene coupling of pentafluorophenylalkynes may be useful in the syntheses of pentafluorophenyl-substituted oligomers and polymers. Diyne **8**, synthesized by the method outlined in Scheme 7, is moderately soluble in dichloromethane and toluene, and soluble in THF. The zirconocene coupling of **8** in THF afforded insoluble zirconium-containing polymers. Although this polymer is depicted in Scheme 7 as having solely $\beta\beta$-C_6F_5 substitution of the zirconacyclopentadiene ring, studies with model alkyne **1c** suggest that up to 15% of these linkages are actually $\alpha\beta$-substituted. However, given the likely conjugation lengths for these polymers,[68] it is expected that the electronic properties should be dominated by regioselectively coupled segments. This metal-containing species reacted with HCl and S_2Cl_2 to produce butadiene (**9**) and thiophene (**10**) polymers, respectively. Polymers **9** and **10** are slightly to moderately soluble in organic solvents such as toluene, dichloromethane, and THF.

The colors of polymers **9** and **10** are orange and yellow, respectively, and the UV−vis spectra of these polymers exhibit λ_{max} values of 382 (**9**) and 340 (**10**) nm. The lower λ_{max} value for polymer **10** is opposite the trend expected for thiophenylenes vs butadienephenylenes,[25] and indicates that the perfluorophenyl pendant groups disrupt the conjugation of **10** more significantly.

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Scheme 7

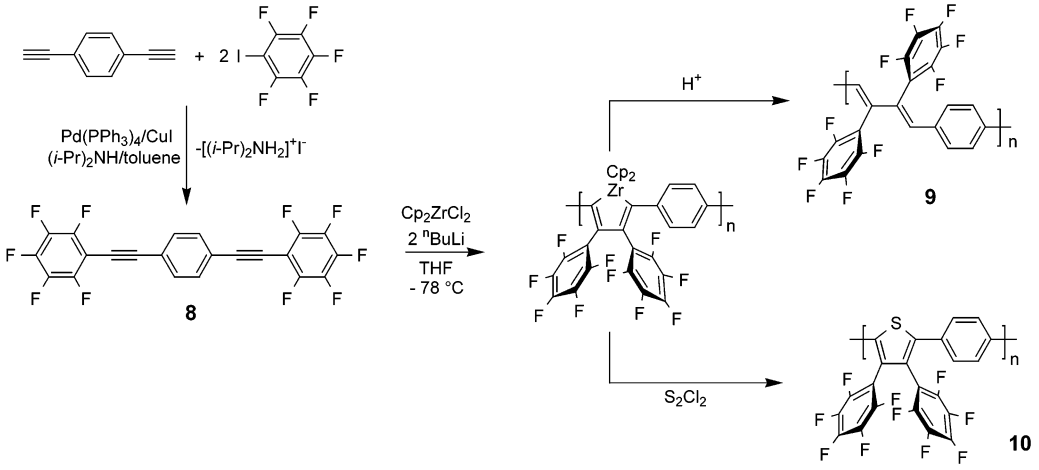

Table 1. Crystallographic Data for the Compounds **2c(*ββ*)**, **4c**, and **7**

	4c	2c(*ββ*)	7
empirical formula	$ZrF_{10}C_{38}H_{20}O_2$	$ZrF_{10}C_{28}H_{16}(C_7H_8)_{0.5}$	$C_{31}H_{16}F_{10}S$
formula weight	789.78	679.71	610.51
crystal color, habit	orange, plate	yellow, bladelike	yellow, block
crystal dimensions	0.51 × 0.10 × 0.10 mm	0.35 × 0.16 × 0.10 mm	0.31 × 0.20 × 0.10 mm
crystal system	monoclinic	monoclinic	triclinic
a, Å	9.515(1)	7.9714(2)	12.5044(8)
b, Å	24.819(3)	34.7343(9)	13.6022(8)
c, Å	16.384(2)	9.7619(1)	16.7412(10)
α, deg	90°	90°	79.390(1)°
β, deg	103.597(2)°	98.123(1)°	68.093(1)°
γ, deg	90°	90°	86.523(2)°
V, Å^3	3761.0(7)	2675.8(1)	2596.6(3)
space group	$P2_1/c$ (#14)	$P2_1/c$ (#14)	$P\bar{1}$ (#2)
Z value	Q	4	4
D_{calc}	1.395 g/cm^3	1.687 g/cm^3	1.562 g/cm^3
F_{000}	1576	1356	1232
μ(MoKα)	3.72 cm^{-1}	5.02 cm^{-1}	2.18 cm^{-1}
radiation	MoKα (l = 0.71069 Å)	MoKα (l = 0.71069 Å)	MoKα (l = 0.71069 Å)
temperature	−99 °C		−86.0 °C
scan type	ω (0.3° per frame)	ω (0.3° per frame)	ω (0.3° per frame)
scan rate (s/frame)	10.0	10.0	10.0
$2\theta_{max}$	49.4°	49.4°	52.3 °
total no. of reflns	16962	11980	14234
no. of unique reflns	2236 (R_{int} = 0.032)	3175(R_{int} = 0.045)	8876 (R_{int} = 0.032)
transmission factors	0.81−0.97	0.54−0.97	0.82−0.96
function minimized	ω (|Fo| − |Fc|)^2	ω (|Fo| − |Fc|)^2	ω (|Fo| − |Fc|)^2
no. with $I \geq n\sigma$(I)	2414 (n = 2)	3271 (n = 3)	4321 (n = 3)
no. variables	341	381	757
reflection/parameter ratio	7.08	8.59	5.71
residuals: R; Rw; rall	0.049; 0.043; 0.111	0.039;0.050,0.060	0.034; 0.032; 0.094
GOF	1.21	1.55	1.04
max Δ/σ	0.05	0.00	0.00
residual density, e$^-$/Å^3	0.4, −0.33	0.47,−0.57	0.28, −0.23

The molecular weights of these polymers (M_w = 9260 for polymer **9**; 11840 for polymer **10**; by gel permeation chromatography with polystyrene standards) are probably limited by the low solubility of the zirconocene-based polymer precursor under the reaction conditions employed. The properties of these polymers are summarized in Table 2, and the absorption and emission spectra are shown in Figure 7.

Table 2. Optical and Molecular Weight Data for Polymers 9 and 10

polymer	M_w/M_n	λ_{max} (nm)	λ_{edge} (nm)	λ_{em} (nm)[a]	E_g (eV)	Φ[b]
9	9260/4860	382	478	485	2.59	0.0122
10	11840/5830	340	438	449	2.76	0.0108

[a] Polymers **9** and **10** were excited at 375 and 340 nm, respectively. [b] Quantum yields for the polymers were obtained by measuring the relative integrated fluorescence intensities compared to a 9,10-diphenylanthracene standard in dichloromethane.

Conclusions

Despite the synthetic utility of the zirconocene coupling of alkynes, there are few studies on the influence of electronic factors on the regioselectivity of this reaction, and likewise little insight into the reaction mechanism. This investigation into the coupling of fluoroaryl substituted alkynes has shown that these electron-withdrawing substituents preferentially adopt the β-position of the resultant zirconacyclopentadiene. This study also demonstrates that there is a significant electronic effect in the regioselectivity of this coupling reaction, and that the transition

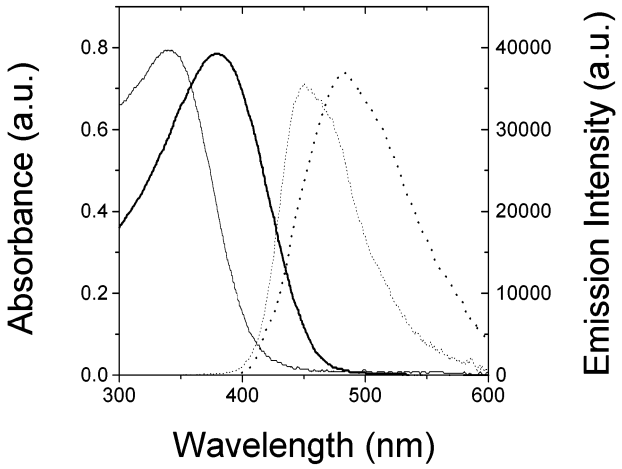

Figure 7. UV-vis and photoluminescent (PL) spectra of polymers **9** (UV−vis: bold solid line; PL: bold dot line) and **10** (UV−vis: thin solid line; PL thin dot line).

state in this reaction does not contain two equally activated alkyne moieties. The nature of the transition state was further examined by DFT calculations, which confirmed that this coupling reaction proceeds via a transition state in which one alkyne is strongly bound to the zirconium center and the other alkyne is only weakly bound. Further mechanistic insight into these reactions was obtained from the previously unreported reversible coupling of some aryl substituted alkynes at 150 °C. This further understanding of the regioselectivity and mechanism of this coupling reaction increases the scope of this reaction in synthesis. For example, the β-directing effect of the fluoroaryl substituents was utilized for the facile synthesis of new conjugated polymers bearing electron-withdrawing pentafluorophenyl groups. The application of these polymers as electron-transport materials is currently under study.

Experimental Section

General Procedures. All manipulations were performed under an inert atmosphere of nitrogen using either standard Schlenk techniques or a glovebox. Dry, oxygen-free solvents were employed throughout. All solvents were distilled from sodium/benzophenone ketyl. Benzene-d_6 was purified by vacuum distillation from Na/K alloy and chloroform-d_1 was distilled from CaH_2. Mass spectra were recorded on a Micromass VG ProSpec instrument (ionization energy: 70 eV). IR spectra were recorded on a Mattson Galaxy Series 3000 spectrometer, and UV−vis spectra were obtained with a HP 8452A spectrophotometer. NMR spectra were recorded on Bruker AMX (300 MHz), Varian Bruker AMX (400 MHz), or Bruker DRX (500 MHz) spectrometers. All chemical shifts are reported in ppm units. For $^{19}F\{^1H\}$ NMR spectra, $C_6H_5CF_3$ was used as the external reference at 0.00 ppm. The molecular weights of the polymers were determined by gel permeation chromatography (GPC; Waters R401 Differential Refractometer Detector; Waters 501 HPLC Pump) with THF as an eluent and polystyrene standards.

Zirconocene dichloride (Strem or Boulder Scientific) and *n*-butyllithium solution (Aldrich) were used as received. The compound 1,4-diethynylbenzene was prepared from 1,4-bis(trimethylsilylethynyl)-benzene by standard procedures,[69] and $Cp_2Zr(py)(Me_3SiC{\equiv}CSiMe_3)$ was prepared by a modification of the original synthesis.[23] Emission spectra were collected by using an Instrument SA/Jobin Yvon-Spex Fluoromax photon-counting fluorimeter equipped with a Xe arc lamp excitation source and a Hamamatsu R928P photomultiplier tube operating at −900 Vdc. Data were collected on deoxygenated solutions (CH_2Cl_2 for standards and samples) having an optical density of 0.08−0.11 (1.0 cm path length) at the excitation wavelength. The excitation energies for photoluminescence spectra were 10 nm lower than the absorption maximum, and excitation spectra were acquired at the emission maximum. No additional corrections were applied. All quantum yield measurements were carried out at a single excitation wavelength (350 nm). Quantum yield (Φ) values are reported relative to a solution of 9,10-diphenylanthracene ($\Phi = 0.90$). Multiple measurements on each sample indicated a precision of 10% for the reported values of Φ.

(*p*-C_6HF_4)C≡C(CH_2)$_4$$CH_3$ (1a). To a mixture of 1-bromo-2,3,5,6-tetrafluorobenzene (3.72 g, 16.2 mmol), $Pd(PPh_3)_4$ (0.502 g, 0.44 mmol), CuI (0.408 g, 2.1 mmol) and diisopropylamine (15 mL) in toluene (30 mL) was added 1-heptyne (1.86 g, 19.4 mmol). The reaction mixture was stirred for 10 h under nitrogen at 95 °C and then the solvent was removed under reduced pressure. The residue was dissolved in hexane (200 mL) and purified by column chromatography on basic alumina using hexane as an eluent to give solid **1a** in 77% yield (1.234 g). ^1H NMR (C_6D_6, 400 MHz, 293 K): δ 6.24 (m, 1H, C_6HF_4), 2.14 (t, J = 9.3 Hz, 2H, $CH_2(CH_2)_3CH_3$), 1.37 (m, 2H, $CH_2CH_2(CH_2)_2CH_3$), 1.23 (m, 4H, $(CH_2)_2(CH_2)_2CH_3$), 0.80 (t, J = 9.4 Hz, 3H, $(CH_2)_4CH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6 MHz): δ 148.5 (m, CC_4F_4CH), 106.2 (m, CC_4F_4CH), 105.3 (t, J = 25 Hz, CC_4F_4CH), 104.7 (t, −C≡C−), 66.4 (t, −C≡C−), 31.5 ($CH_2(CH_2)_3CH_3$), 28.2 ($CH_2CH_2(CH_2)_2CH_3$), 22.9 ($(CH_2)_2CH_2CH_2CH_3$), 19.8 ($(CH_2)_3CH_2CH_3$), 14.1 ($(CH_2)_4CH_3$). $^{19}F\{^1H\}$ NMR (C_6D_6, 376.5 MHz): δ −90.5 (m), −92.0 (m). EIMS showed M^+ = 244. HRMS Calcd for $C_{13}H_{12}F_4$, 244.0875; Found, 244.0870.

(*p*-C_6HF_4)C≡CCH_3 (1b). To a mixture of propyne (1.90 g, 48 mmol) and 1-bromo-2,3,5,6-tetrafluorobenzene (2.512 g, 11 mmol) in toluene (21 mL) were added $Pd(PPh_3)_4$ (0.347 g, 0.30 mmol), CuI (0.288 g, 1.52 mmol) and diisopropylamine (9 mL). The reaction mixture was stirred for 24 h under an inert atmosphere at 80 °C. The solution was then filtered and purified by chromatography on basic alumina using hexane as an eluent. After the solvent was removed, the remaining solid was sublimed under vacuum to provide 1.24 g of a pale yellow crystalline solid (60% yield). ^1H NMR (C_6D_6, 400 MHz): δ 6.15 (m, 1H, C_6HF_4), 1.51 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6 MHz): δ 147.2 (m, CC_4F_4CH), 106.1 (t, J = 10, CC_4F_4CH), 105.4 (t, J = 20 Hz, CC_4F_4CH), 100.3 (t, −C≡C−), 66.5 (t, −C≡C−), 4.0 (CH_3). $^{19}F\{^1H\}$ NMR (C_6D_6, 376.5 MHz, 293 K): δ −90.7 (m), −91.9 (m). EIMS showed M^+ = 188, HRMS Calcd for $C_9H_4F_4$, 188.0249; Found, 188.0248.

(C_6F_5)C≡CPh (1c). To a mixture of phenylacetylene (1.04 g, 10 mmol) and pentafluoro-iodobenzene (3.0 g, 10 mmol) in toluene (30 mL) were added $Pd(PPh_3)_4$ (0.346 g, 0.30 mmol), CuI (0.180 g, 0.947 mmol) and diisopropylamine (9 mL). The reaction mixture was stirred for 24 h under an inert atmosphere at 80 °C. The solution was filtered and evaporated to dryness. Sublimation at 70 °C under vacuum (1×10^{-2} mmHg) provided 1.92 g of white solid (70% yield). ^1H NMR ($CDCl_3$, 400 MHz, 293 K): δ 7.62 (d, 2H, ArH), 7.43(m, 3H, ArH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 147.2 (d, J = 25 Hz, C_5F_5C), 141.3 (d, J = 25 Hz, C_5F_5C), 137.5 (d, J = 25 Hz, C_5F_5C), 131.7 (s, ArC−H), 129.5 (s, p-ArCH), 128.4 (s, ArC−H), 121.5 (s, ArC), 101.5 (s, C≡C), 100.3 (m, C_5F_5C), 72.9 (s, C≡C). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 376.5 MHz, 293 K): δ −19.8 (m), −28.8 (t, J = 24 Hz). −45.6 (m). EIMS showed M^+ = 268. HRMS Calcd for $C_{14}H_5F_5$, 268.0311; Found, 268.0309.

(*p*-$CF_3C_6H_4$)C≡C(*p*-MeC_6H_4) (1d). This compound was prepared by the same method as **1a** using 4-trifluoromethyl-iodobenzene and tolylacetylene. A white solid was obtained after recrystallization from hexane. Yield: 73%. ^1H NMR (C_6D_6, 400 MHz): δ 7.40 (d, J = 8.1 Hz, 2H, ArH), 7.20 (d, J = 8.1 Hz, 2H, ArH), 7.08 (d, J = 8.1 Hz, 2H, ArH), 6.77 (d, J = 8.1 Hz, 2H, ArH), 1.92 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6 MHz): δ 139.58 (s, ArC−H), 132.35 (s, ArC−H),

(69) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*; 2nd ed.; John Wiley and Sons: New York, 1991.

130.31 (s, ArC), 129.99 (s, ArC), 129.93 (s, ArC), 128.27 (t, J = 28 Hz, CF_3Ar-o−H), 125.86 (q, J = 28 Hz, CF_3Ar-m−H), 123.66 (t, J = 272 Hz, CF_3ArC), 120.47 (s, ArC), 93.02 (s, C≡C), 88.43 (s, C≡C), 21.67 (s, CH_3). $^{19}F\{^1H\}$ NMR (C_6D_6, 376.5 MHz): δ 0.33. EIMS showed M^+ = 260. HRMS Calcd for $C_{16}H_{11}F_3$, 260.0813; Found, 260.0808.

Cp_2ZrC_4-3,4-(C_6HF_4)$_2$-2,5-(C_5H_{11})$_2$ (2a). A 100 mL round-bottom flask was charged with Cp_2ZrCl_2 (0.300 g, 1.03 mmol) and THF (40 mL). The solution was cooled to −78 °C and *n*-BuLi (1.2 mL, 1.92 mmol, 1.6 M in hexane) was added. Then a solution of **1a** (0.512 g, 2.09 mmol) dissolved in THF (15 mL) was added and the resulting solution was stirred until the cooling bath reached room temperature (over 6 h). The solvent was removed and the residue was extracted with pentane (3 × 15 mL). Yellow crystals (0.43 g, 64% yield) were obtained from this pentane solution at a temperature of −40 °C. ^1H NMR (C_6D_6, 400 MHz): δ 6.13 (m, 1H, C_6HF_4), 6.07 (s, 5H, Cp), 2.04 (t, J = 7.6 Hz, 2H, $-CH_2(CH_2)_3CH_3$), 1.06 (m, 6H, $-CH_2(CH_2)_3CH_3$), 0.82 (t, J = 7.2 Hz, 3H, $-CH_2(CH_2)_3CH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6 MHz): δ 199.9 (ZrC_2), 144.6 (m, CC_4F_4CH), 122.6 (C_6F_4H), 120.5 (ZrC=*C*), 111.3 (Cp), 103.9 (t, J = 20 Hz, C_5F_4CH), 39.9 ($-CH_2(CH_2)_3CH_3$), 32.6 ($-CH_2CH_2(CH_2)_2CH_3$), 30.5 ($-(CH_2)_2CH_2CH_2CH_3$), 22.7 ($-(CH_2)_3CH_2CH_3$), 14.1 ($-(CH_2)_4CH_3$). $^{19}F\{^1H\}$ NMR (C_6D_6, 376.5 MHz): δ −90.0 (m), −90.4 (m). EIMS showed M^+ = 708.

Cp_2ZrC_4-3,4-(C_6HF_4)$_2$-2,5-(CH_3)$_2$ (2b). The compound was prepared by the same method used for **2a**, employing the alkyne **1b**. Yellow crystals were obtained in 72% yield by cooling a saturated pentane solution to −40 °C. ^1H NMR (C_6D_6, 400 MHz): δ 6.13 (m, 1H, C_6HF_4), 5.92 (s, 5H, Cp), 1,42 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6 MHz): δ 194.6 (ZrC_2), 144.6 (m, CC_4F_4CH), 122.9 (C_6F_4H), 112.3 (ZrC=*C*), 111.5 (Cp), 103.8 (t, J = 25 Hz, C_5F_4CH), 22.2 (CH_3). $^{19}F\{^1H\}$ NMR (C_6D_6, 376.5 MHz): δ −89.6 (m), −90.2 (m).

$Cp_2ZrC_4(C_6F_5)_2Ph_2$ (2c($\beta\beta$)). Method (a) The compound was prepared by the same method used for **2a**, except that toluene (30 mL) was used instead of pentane to extract the product from the crude reaction mixture. The toluene solution was evaporated to dryness and the remaining solid was rinsed with 5 mL of pentane and dried. This yellow solid contains ca. 15% of the $\alpha\beta$ isomer as an impurity. Yellow crystals of the $\beta\beta$ isomer were obtained in 75% yield from slow evaporation of a diethyl ether solution at room temperature. ^1H NMR (C_6D_6, 400 MHz): δ 6.9−6.95 (m, 4H, C_6H_5), 6.65−6.75 (m, 6H, C_6H_5), 5.92 (s, 10H, Cp). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.77 MHz): δ 202.9 (ZrC_2), 147.5 (ArC), 145.1 (m, C_6F_5), 143.2 (m, C_6F_5), 141.0 (m, C_6F_5), 136.3 (m, C_6F_5), 128.5 (ArC−H), 124.9 (ArC−H), 124.5 (ArC−H), 114.1 (ZrC=*C*), 113.1 (Cp). $^{19}F\{^1H\}$ NMR (C_6D_6, 376.5 MHz): δ −4.2 (m, 2F, p−C−F), −11.9 (t, J = 18.8 Hz, 4F, o−C−F), −28.4 (m, 4F, m−C−F). Anal. Calcd for $C_{38}H_{20}F_{10}Zr$: C, 60.23; H, 2.66. Found: C, 58.86; H, 2.38.

Method b) $Cp_2Zr(py)(Me_3SiC{\equiv}CSiMe_3)$ (0.210 g, 0.42 mmol) and **1c** (0.230 g, 0.86 mmol) were separately dissolved in 10 mL of pentane. The two solutions were combined at 0 °C and the resulting reaction solution was stirred at this temperature for 6 h. The solution was then allowed to warm to room temperature and was stirred for 12 h. The yellow precipitate was isolated by filtration, washed with pentane, and dried under high vacuum. Yield: 0.163 g (51%). This product contained ∼20% of the $\alpha\beta$-isomer. ^1H NMR of $\alpha\beta$ isomer (C_6D_6, 400 MHz): δ 6.95−7.0 (m, 4H, C_6H_5), 6.80−6.85 (m, 6H, C_6H_5), 6.01 (s, 10H, Cp). $^{19}F\{^1H\}$ NMR of $\alpha\beta$ isomer (C_6D_6, 376.5 MHz): δ −3.1 (m, 1F, p−C−F), −3.8 (m, 1F, p−C−F), −6.3 (t, J = 22.5 Hz, 2F, o−C−F), −10.4 (t, J = 22.5 Hz, 2F, o−C−F), −27.3 (m, 2F, m−C−F), −28.5 (m, 2F, m−C−F).

$Cp_2ZrC_4(C_6H_4Me)_2(C_6H_4CF_3)_2$ (2d($\beta\beta$) and 2d($\alpha\beta$)). This compound was prepared as a mixture of the symmetrical ($\beta\beta$) and the unsymmetrical ($\alpha\beta$) isomers. Method (a). The compound was prepared by the same method used for **2a**, from the alkyne **1d**. Trituration of the crude reaction mixture with benzene yielded an orange powder consisting of three compounds: Unreacted alkyne (∼20%), the $\beta\beta$ isomer (∼40%) and the $\alpha\beta$ isomer (∼40%). Ratios were obtained by integration of the peaks in the $^{19}F\{^1H\}$ NMR spectrum and are in agreement with the integration of the methyl peaks in the ^1H NMR spectrum, which are not completely resolved. ^1H NMR (C_6D_6, 400 MHz): δ 6.3−7.4 (several phenyl-H signals of the different compounds), 5.98 and 5.93 (Cp ∼1:1), 2.04 (CH_3 of $\beta\beta$ and $\alpha\beta$ isomer), 1.79 (CH_3 $\alpha\beta$ isomer). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 376.5 MHz): δ 0.99 ($\alpha\beta$ isomer, 20%), 0.73 ($\alpha\beta$ isomer, 20%), 0.58 ($\beta\beta$ isomer, 40%), 0.04 (**1d** 20%). EIMS showed M^+ = 740. HRMS Calcd for $C_{42}H_{32}F_6{}^{90}Zr$, 740.1455; Found, 740.1440. HRMS Calcd for $C_{42}H_{32}F_6{}^{91}Zr$, 741.1465; Found, 741.1466. HRMS Calcd for $C_{42}H_{32}F_6{}^{92}Zr$, 742.1459; Found, 742.1521.

Method (b) $Cp_2Zr(py)(Me_3SiC{\equiv}CSiMe_3)$ (18.8 mg, 0.038 mmol) and **1d** (20 mg, 0.076 mmol) were dissolved in benzene-d_6 (0.6 mL) in an NMR tube. The solution was left overnight at room temperature. The product mixture was similar to that observed using method (a), but also included 5% of a third species, which was assigned as the $\alpha\alpha$ isomer: $^{19}F\{^1H\}$ (C_6D_6, 376.5 MHz) δ 1.07 ($\alpha\beta$ isomer 45%), 1.05 ($\alpha\alpha$ isomer, 5%), 0.73 ($\alpha\beta$ isomer 45%), 0.58 ($\beta\beta$ isomer, 50%). ^1H NMR (C_6D_6, 400 MHz), select peaks: δ 5.98 (s, 50%, $\beta\beta$ isomer, CpH) and 5.93 (s, 45%, $\alpha\beta$ isomer, CpH 45%), 5.88 (s, 5%, $\alpha\alpha$ isomer, CpH) 2.04 (overlapping s, CH_3 of $\beta\beta$ and $\alpha\beta$ isomers), 1.79 (s, CH_3 $\alpha\beta$ isomer), 1.81 (s, $\alpha\alpha$ isomer, CH_3).

(C_5H_{11})CHC(C_6HF_4)C(C_6HF_4)CH(C_5H_{11}) (3a). A 100 mL round-bottom flask was charged with compound **2a** (0.259 g, 0.37 mmol) and THF (20 mL). Then 6 N HCl (4 mL) was added to the flask and the mixture was stirred for 2 h. The solvent was removed and the residue was recrystallized from hexane to afford a colorless product in a yield of 78%. ^1H NMR (C_6D_6, 400 MHz): δ 6.32 (m, 1H, C_6HF_4), 5.56 (t, J = 7.2 Hz, 1H, $CH_3(CH_2)_4$ C*H*=C), 1.73 (q, J = 7.2 Hz, 2H, $CH_3(CH_2)_3CH_2CH{=}C$), 1.01 (m, 6H, $CH_3(CH_2)_3CH_2CH{=}C$), 0.73 (t, J = 7.2 Hz, 3H, $CH_3(CH_2)_3CH_2CH{=}C$). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6 MHz): δ 145.1 (m, CC_4F_4CH), 135.7 ((C_5H_{11})CH=*C*), 127.6 ((C_5H_{11})-*C*H=C), 118.8 (t, CC_4F_4CH), 105.8 (t, J = 22 Hz, CC_4F_4CH), 31.4 ($CH_3(CH_2)_3CH_2CH{=}C$), 30.2 ($CH_3(CH_2)_2CH_2CH_2CH{=}C$), 28.6 ($CH_3CH_2CH_2(CH_2)_2$ CH=C), 22.5 ($CH_3CH_2(CH_2)_3CH{=}C$), 13.9 ($CH_3(CH_2)_4$-CH=C). $^{19}F\{^1H\}$ NMR (C_6D_6, 376.5 MHz): δ −90.2 (m), −91.9 (m).

MeCHC(C_6HF_4)C(C_6HF_4)CHMe (3b). This compound was prepared by the same method used for **3a**, from **2b**. The pure colorless product was obtained by recrystallization from pentane in a yield of 52%. ^1H NMR (C_6D_6, 400 MHz): δ 6.32 (m, 1H, C_6HF_4), 5.42 (q, J = 6.8 Hz, 1H, $CH_3CH{=}C$), 1.20 (d, 3H, J = 6.4 Hz, $CH_3CH{=}C$). $^{13}C\{^1H\}$ NMR (C_6D_6, 100,6 MHz): δ 145.1 (m, CC_4F_4 CH), 129.7 ($CH_3CH{=}C$), 128.6 ($CH_3CH{=}C$), 118.3 (t, CC_4F_4CH), 105.7 (t, J = 23 Hz, CC_4F_4CH), 15.0 ($CH_3CH{=}C$). $^{19}F\{^1H\}$ NMR (C_6D_6, 376.5 MHz): δ −89.9 (m), −91.9 (m).

PhCHC(C_6F_5)C(C_6F_5)CHPh (3c). A 250 mL Schlenk flask was charged with Cp_2ZrCl_2 (0.876 g, 3.0 mmol) and THF (60 mL). The solution was cooled to −78 °C and *n*-BuLi (3.75 mL, 6.0 mmol, 1.6 M in hexane) was added. Then a solution of **1c** (1.608 g, 6.0 mmol) dissolved in THF (30 mL) was added and the resulting reaction solution was stirred until the cooling bath reached room temperature (ca. 6 h). The reaction mixture was then heated for 1 h at 65 °C. The solution was then treated with 10 mL of aqueous HCl (6 N) at 0 °C, and then extracted with hexane (2 × 50 mL). The compound was purified by flash column chromatography and sublimed at 85 °C under 2−10 mmHg. Yield: 1.34 g (84%). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.20 (m, 3H, ArH), 6.92 (m, 2H, ArH), 6.65 (s, 1H, C*H*=C). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100,6 MHz): δ 144.2 (dm, J = 25 Hz, CC_5F_5), 141.4 (dm, J = 25 Hz, C_5F_5), 138.0 (dm, J = 25 Hz, C_5F_5), 135.3 (s, C_5H_5C), 135.2 (s, C_5H_5C), 128.3 (s, C_5H_5C), 128.2 (s, C=C), 127.9 (s, C_5H_5C), 126.9 (s, C=C), 112.4 (m, C_6F_5). $^{19}F\{^1H\}$NMR ($CDCl_3$, 376.5 MHz): δ −20.0 (d, J = 7.1 Hz), −34.3 (t, J = 3.5 Hz), −42.1 (m). EIMS showed M^+ = 538 (100%). HRMS Calcd for $C_{28}H_{12}F_{10}$, 538.0779; Found, 538.0780.

3d(ββ) and 3d(αβ). These compounds were synthesized by the same method used for **3a**, from **2d(ββ)** and **2d(αβ)**. The product was purified by flash column chromatography (silica/pentane:diethyl ether = 200:1). A first fraction enriched with the αβ isomer was obtained, and a mixed fraction containing the αβ isomer and the symmetrical isomer in a ratio of 1:2 was eluted second. ^{1}H NMR of αβ isomer ($CDCl_3$, 400 MHz): δ 7.66 (d, J = 8.3 Hz, 2H, H^f), 7.43 (d, J = 8.0 Hz, 2H, H^e), 7.26 (d, J = 8.0 Hz, 2H, H^d), 7.21 (d, J = 7.8 Hz, 2H, H^a), 7.14 (d, J = 7.8 Hz, 2H, H^b), 6.86 (d, J = 8.2 Hz, 2H, H^h), 6.83 (d, J = 8.2 Hz, 2H, H^c), 6.60 (d, J = 8.0 Hz, 2H, H^g), 6.40 (s, 1H, H^k), 6.15 (s, 1H, H^i), 2.41 (s, 3H, CH_3^m), 2.21 (s, 3H, CH_3^e). ^{19}F{^{1}H} NMR of αβ isomer ($CDCl_3$, 376.5 MHz): δ 0.43 (s, 3F, CF_3), 0.21 (s, 3F, CF_3). ^{1}H NMR of symmetric ββ isomer ($CDCl_3$, 400 MHz): δ 7.67 (d, J = 8.0 Hz, 4H, H^d), 7.45 (d, J = 8.0 Hz, 4H, H^c), 6.88 (d, J = 8.1 Hz, 4H, H^a), 6.62 (d, J = 8.1 Hz, 4H, H^b), 6.26 (s, 2H, H^e), 2.23 (s, 6H, H^f). ^{13}C{^{1}H} NMR ββ isomer ($CDCl_3$, 125.76 MHz): δ 143.59, 142.78, 137.19 (C^{ipso}−CH_3), 133.46, 132.19 (C−H^e), 130.87 (C−H^c), 129.35 (C−H^b), 128.80 (C−H^a), 125.84 (q, J = 4 Hz, C−H^d), 123.15 (t, J = 342 Hz, CF_3), 21.07 (C−H$^f_3$). ^{13}C{^{1}H} NMR αβ isomer ($CDCl_3$, 125.76 MHz): δ 124.9 (C−H^d), 125.2 (C−H^f), 125.8 and 125.8 (C−H^h), 125.9, 125.9 and 125.9 (C−H^c, C−H^g, C−H^i), 130.0 (C−H^a), 130.1 (C−H^b), 130.2 (C−H^e), 130.7 (C−H^k). ^{19}F{^{1}H} NMR of ββ isomer ($CDCl_3$, 376.5 MHz): δ 0.43 (s, 6F, CF_3). Resonances were assigned using inverse C−H correlation (1 bond HMQC) and a NOESY experiment. EIMS of the mixture showed M^+ = 522. HRMS Calcd for $C_{32}H_{24}F_6$, 522.1782; Found, 522.1778.

SC$_4$-2,5-Ph$_2$-3,4-(C$_6$F$_5$)$_2$ (4c). The compound was prepared by a method analogous to that used for **3c**, except that instead of hydrolysis the reaction mixture was quenched with 1 equiv of S_2Cl_2 and stirred for an additional 6 h. Afterward the volatile materials were removed by vacuum transfer and the residue was extracted into hexane (2 × 50 mL). The pure yellow product was obtained by crystallization from pentane at −40 °C in 76% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35 (m, 3H, C_6H_5), 7.28 (m, 2H, C_6H_5). ^{13}C{^{1}H} NMR ($CDCl_3$, 100,6 MHz): δ 44.5 (dm, J = 25 Hz, CC_5F_5), 144.3 (s, SC=C), 141.1 (dm, J = 25 Hz, CC_5F_5), 139.2 (dm, J = 22 Hz, CC_5F_5), 132.3 (s, CC_5H_5), 128.9 (s, CC_5H_5), 128.8 (s, CC_5H_5), 128.2 (s, CC_5H_5), 122.6 (s, SC=C), 109.9 (m, C_6F_5). ^{19}F{^{1}H} NMR ($CDCl_3$, 376.5 MHz): δ −20.3 (d, J = 3.5 Hz), −34.0 (t, J = 3.5 Hz), −42.4 (m). EIMS showed M^+ = 568 (100%). HRMS Calcd for $C_{28}H_{10}F_{10}S$, 568.0344; Found, 568.0343. IR (KBr): 1500s, 990s cm^{-1}.

1,2-(CO$_2$Me)$_2$-4,5-(C$_6$F$_5$)$_2$-3,6-(C$_6$H$_5$)$_2$C$_6$ (5c). This compound was prepared by a method similar to that used for **3c**, except that instead of hydrolysis the reaction mixture was cooled to 0 °C and one equiv of $MeO_2CC{\equiv}CCO_2Me$ and CuCl were added. The mixture was stirred at room temperature for 2 h and then heated for 8 h at 65 °C. The reaction mixture was hydrolyzed by adding aqueous HCl (3N, 10 mL). The product was extracted into hexane (2 × 50 mL) and purified by silica gel column chromatography using hexane/ether (50/1) as eluting solvents. Yield: (55%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28 (m, 3H, C_6H_5), 7.14 (m, 2H, C_6H_5), 3.52 (s, 3H, OCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100,6 MHz): δ 167.1 (s, CO_2CH_3), 143.5 (dm, J = 25 Hz, CC_5F_5), 141.7 (s, C_6−C_6F_5), 141.2 (dm, J = 24 Hz, CC_5F_5), 136.8 (dm, J = 25 Hz, CC_5 F_5), 136.5 (s, C_6−C_6H_5), 134.7 (s, C_6−CO_2Me), 130.0 (s, C_6H_5), 128.4 (s, CC_5H_5), 128.1 (s, CC_5H_5), 128.0 (s, C_5H_5), 112.3 (m, C_6F_5), 52.6 (s, CO_2CH_3). ^{19}F{^{1}H} NMR ($CDCl_3$, 376.5 MHz): δ −20.7 (m), −30.2 (t, 24 Hz), −44.1 (m). EIMS showed M^+ = 678 (100%). HRMS Calcd for $C_{34}H_{16}F_{10}O_4$, 678.0889; Found, 678.0898.

[(C$_6$F$_5$)C≡CCH$_2$]$_2$CH$_2$ (6). A solution of 1,6-heptadiyne (1.567 g, 0.017 mol) and C_6F_5I (10.0 g, 0.034 mol, 2 equiv) in 200 mL of Et_3N was added to a mixture of solid $Pd(PPh_3)_4$ (1.00 g, 0.025 equiv) and CuI (0.32 g, 0.05 equiv) at room temperature under a nitrogen atmosphere. The solution was stirred and refluxed for 24 h. The solvent was then removed under vacuum and the remaining solid was extracted into 300 mL of pentane and filtered in air. The pentane solution was then evaporated to dryness and the solid that remained was sublimed onto a water-cooled coldfinger under full vacuum at a bath temperature of 110 °C, which yielded 1,7-bis(pentafluorophenyl)-1,6-heptadiyne (4.85 g, 67%) as a white solid (mp 70−71 °C). ^{1}H NMR (chloroform-d, 400 MHz, 295 K): δ 1.97 (p, $^3J_{HH}$ = 7.0 Hz, 2H, $CH_2CH_2CH_2$), 2.69 (t, $^3J_{HH}$ = 7.0 Hz, 4H, C≡CCH_2). ^{19}F{^{1}H} NMR (chloroform-d, 376.32 Hz, 295 K): δ −74.5 (m, o-C_6F_5), −91.5 (m, p-C_6F_5), −99.7 (m, m-C_6F_5). ^{13}C{^{1}H} (chloroform-d, 100.56 Hz, 295 K): δ 18.8 (s, C≡CCH_2), 26.7 (s, $CH_2CH_2CH_2$), 65.6 (m, C_6F_5C≡C), 100.3 (m, ipso-C_6F_5), 102.2 (m, C_6F_5C≡C), 137.6 (dm, m-C_6F_5), 141.1 (dm, p-C_6F_5), 147.4 (ddd, o-C_6F_5). UV−vis: 240 (43 000), 252 (47 000), 274 (sh, 2600). IR (KBr, cm^{-1}) 2249 m (C≡C), 1652 m, 1629 m, 1509 s, 1520 s, 1051 s, 990 s, 864 w, 822 w. Anal. Calcd for $C_{19}H_6F_{10}$: C, 53.79; H, 1.43. Found: C, 53.92; H, 1.46. EI−MS m/z 424.

Cp$_2$ZrC$_4$(2,5-C$_6$F$_5$)(CH$_2$)$_3$ (7). The two solids 1,7-bis(pentafluorophenyl)-1,6-heptadiyne (0.976 g, 2.30 mmol) and $Cp_2Zr(py)(Me_3SiC{\equiv}CSiMe_3)$ (1.08 g, 1 equiv) were combined in a 250 mL Schlenk flask under a nitrogen atmosphere and cooled to −78 °C in a dry ice bath. Hexanes (40 mL) was added via cannula transfer and the solution was stirred. The dry ice bath was removed and the solution was allowed to warm to room temperature, which resulted in the formation of a yellow precipitate. After 1 h at room temperature, the solution was removed under vacuum and an additional 20 mL of hexanes was added to the remaining solid, and then removed by cannula filtration. The yellow solid was dried under vacuum (1.22 g, 82.4%). Single crystals for X-ray crystallographic analysis were obtained by slow evaporation of a toluene solution. ^{1}H NMR (benzene-d_6, 400 MHz, 295 K): δ 1.20 (p, $^3J_{HH}$ = 7.1 Hz, 2H, $CH_2CH_2CH_2$), 2.00 (t, $^3J_{HH}$ = 7.0 Hz, 4H, C=CCH_2), 5.81 (s, 10H, Cp). ^{19}F{^{1}H} NMR (benzene-d_6, 376.32 Hz, 295 K): δ −78.8 (m, o-C_6F_5), −98.0 (t, p-C_6F_5), −99.7 (m, m-C_6F_5). ^{13}C{^{1}H} (benzene-d_6, 100.56 Hz, 295 K): δ 21.6 (s, $CH_2CH_2CH_2$), 36.3 (s, C=CCH_2), 111.7 (s, η^5-C_5H_5), 124.1 (t, J_{CF} = 41 Hz, $ipso$-C_6F_5), 133.9 (s, C=C), 138.1 (m, p-C_6F_5), 138.1 and 142.7 (m, o-C_6F_5 and m-C_6F_5), 166.1 (s, C=C). Anal. Calcd for $C_{29}H_{16}F_{10}Zr$: C, 53.95; H, 2.50. Found: C, 54.13; H, 2.48.

Heating of Cp$_2$ZrC$_4$Ph$_4$ with 1d. A 1 mL benzene-d_6 solution of of the bis(cyclopentadienyl)1,2,3,4-tetraphenylzirconacylopentadiene (29 mg, 0.050 mmol) and alkyne **1d** (15 mg, 0.056 mmol) were combined in an NMR tube equipped with a Teflon valve and the tube was sealed. The tube was then heated in a 150 °C oil bath. The tube was removed after 1, 15, and 72 h, and the ^{1}H and ^{19}F{^{1}H} NMR spectra were obtained. After 1 h a 4% conversion of **1d** was observed into 2 new products. ^{19}F{^{1}H} NMR after 1 h (benzene-d_6, 376.32 Hz, 295 K): δ 0.03 (**1d**), 0.76 (70%, β), 1.12 (30%, α). Continued heating provided a thermodynamic mixture of these two new products as well as the αα, αβ, and ββ isomers of **2d**. ^{19}F{^{1}H} NMR after 72 h (benzene-d_6, 376.32 Hz, 295 K): δ 0.03 (**1d**), 0.57 (**2d**-ββ), 0.73 (**2d**-αβ), 0.76 (β), 1.04 (**2d**-αβ), 1.07 (**2d**-αα) 1.12 (α). The experiment was repeated with 10 equiv of **1d**. The initial products and rate of reaction remained the same; however extended heating over 72 h led to a mixture containing only the αα, αβ and ββ isomers of **2d**. ^{19}F{^{1}H} NMR after 72 h (benzene-d_6, 376.32 Hz, 295 K): δ 0.03 (**1d**), 0.57 (18%, **2d**-ββ), 0.73 (59%, **2d**-αβ), 1.04 (59%, **2d**-αβ), 1.07 (23%, **2d**-αα).

Heating of 2d(αβ)/2d(ββ) with with 1c. Solid $C_6F_5C{\equiv}CPh$ (8.2 mg, 0.030 mmol) was added to a 1 mL benzene-d_6 solution of a 1:1 mixture of **2d(αβ)** and **2d(ββ)**, which was prepared by combining $Cp_2Zr(Me_3SiC{\equiv}CSiMe_3)(py)$ (10.1 mg, 0.021 mmol) with **1d** (11.2 mg, 0.043 mmol). The solution was transferred to an NMR tube equipped with a Teflon valve and the tube was sealed. The solution was then heated in a 150 °C oil bath. The tube was removed after 2 h, and the ^{1}H and ^{19}F{^{1}H} NMR spectra were obtained. Along with unreacted starting material and a small amount of **2c**, two new products were observed in a 1:1 ratio: $Cp_2Zr(C_4)$-2-C_6H_4Me-3-$C_6H_4CF_3$-4-C_6F_5-5-Ph (labeled β[CF_3]β[C_6F_5]) and $Cp_2Zr(C_4)$-2-$C_6H_4CF_3$-3-C_6H_4Me-4-C_6F_5-5-Ph (labeled α[CF_3]β[C_6F_5]). ^{19}F{^{1}H} NMR, select peaks, after 2 h (benzene-d_6, 376.32 Hz, 295 K): δ 0.95 (s, 50%, α[CF_3]β[C_6F_5]),

0.47 (s, 50%, β[CF_3]β[C_6F_5]), −77.05 (overlapping m, β[CF_3]β[C_6F_5] and α[CF_3]β[C_6F_5] *o*-C_6F_5), −94.65 and −94.95 (m, β[CF_3]β[C_6F_5] and α[CF_3]β[C_6F_5] *p*-C_6F_5), −101.65 and −101.95 (m, β[CF_3]β[C_6F_5] and α[CF_3]β[C_6F_5] *m*-C_6F_5). ^{1}H NMR, select peaks, (benzene-d_6, 400 MHz, 295 K): δ 1.76 and 1.99 (s, 1:1, β[CF_3]β[C_6F_5] and α[CF_3]β[C_6F_5] *p*-$C_6H_4CH_3$).

1,4-[(C_6F_5)C≡C]$_2$$C_6H_4$ (8). To a mixture of pentafluoroiodobenzene (11.76 g, 40.0 mmol), Pd(PPh_3)$_4$ (0.98 g, 0.84 mmol), CuI (0.20 g, 1.0 mmol) and diisopropylamine (15 mL) in toluene (120 mL) was added 1,4-bisethynylbenzene (2.52 g, 20.0 mmol). The reaction mixture was stirred for 48 h under nitrogen at 95 °C and then the solvent was removed under reduced pressure. To this residue was added water (100 mL), and the resulting mixture was extracted with a mixture of hexane/dichloromethane (1:1, 2 × 100 mL). The solvents were removed and the residue was purified by silica gel column chromatography using hexane/ether/methylene chloride (2/1/1) as an eluent. The product was isolated as a pale yellow solid in 65% yield (6.6 g). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60 (s). ^{13}C{^{1}H} NMR ($CDCl_3$, 124 Hz): δ 147.0 (d, J = 25 Hz, C_5F_5C), 141.5 (d, J = 25 Hz, C_5F_5C), 137.8 (d, J = 25 Hz, C_5F_5C), 131.9 (s, Ar*C*-H), 122.7 (s, p-Ar*C*), 100.6 (s, C≡C), 100.0 (m, C_5F_5C), 75.4 (s, C≡C). ^{19}F{^{1}H} NMR (chloroform-d_1, 376.5 MHz): δ −20.2 (m), −29.8 (t, J = 24 Hz), −46.0 (m). IR (KBr) 2223 w C≡C), 1524 s, 1498 s (aromatic CC), 1116 m (CF), 999 s, 996 m, 836 m, 685 m cm^{-1}. EIMS showed M^+ = 458. HRMS Calcd for $C_{22}H_4F_{10}$, 458.0153; Found, 458.0149.

[C_6H_4CH=C(C_6F_5)C(C_6F_5)=CH]$_n$ (9). The polymer was prepared by a method similar to that used for compound **3a**. After hydrolysis, an orange solid was precipitated by the addition of methanol to the solution. The polymer was further purified by precipitation from THF by the addition of methanol and dried under vacuum. Yield: 80%. GPC: M_n/M_w = 4860/9280. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.6−7.0 (br, 4 H, C_6H_4), 6.4−6.6 (br, 2H, C*H*=C−C_6F_5). IR (KBr) 1651 m (C=C conjugated with aryl), 1603 (C=C conjugated with C=C and aryl), 1500 s, 1498 s (aromatic C=C), 1120 s (CF), 977 s, 940 m, 885 m, 837 m, 812 m, 551 m cm^{-1}.

[−C_6H_4C=C(C_6F_5)C(C_6F_5)=CS]$_n$ (10). The polymer was prepared by a method analogous to that used for compound **4c.** After work up, a yellow-green solid was isolated from THF/methanol in a yield of 74%. The ^{1}H NMR spectrum in $CDCl_3$ contained no vinylic resonances. GPC: M_n/M_w = 5830/11,840. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.16−7.3 (br, C_6H_4). IR (KBr) 1652 w (C=C conjugated with aryl), 1521 s, 1496 s (aromatic C=C), 1097 m (CF), 991 s, 918 m, 732 m cm^{-1}.

Calculations

Ab initio DFT calculations were performed using the hybrid functional B3LYP[70] method with the Jaguar[71] package. The basis functions and effective core potentials used were the LACVP* set,[72] provided in the Jaguar program. The ground-state structures were optimized in C_2, C_s, and C_1 symmetry. The C_β−C_β bond length was then incrementally increased from the ground-state structure, and the geometry along each point in the coordinate search was optimized in C_1 symmetry. In the case of the MeC≡CMe coupling, this provided an initial point to perform a QST guided transition state search; the resulting structure was not qualitatively significantly different from the initial search structure. In the case of the PhC≡C(C_6F_5) coupling, the QST guided search failed to find a transition state, so the approximate transition state used is that found using the coordinate search.

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Supporting Information Available: ^{1}H NOESY and C−H correlation spectra for the two isomers of **3d($\beta\beta$)** and **3d($\alpha\beta$)**. Tables of crystal data collection and refinement parameters, coordinates, bond distances, angles, and anisotropic displacement parameters for **2c($\beta\beta$)**, **4c** and **7** . Coordinates for DFT geometry optimizations (66 pages, print/PDF). This material is contained in many libraries on microfiche which immediately follows this article in the microfilm version of the journal and can be ordered from ACS or downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions. This material is available free of charge via the Internet at http://pubs.acs.org.

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