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Mesityl Alkyne Substituents for Control of Regiochemistry and Reversibility in Zirconocene Couplings: New Synthetic Strategies for Unsymmetrical Zirconacyclopentadienes and Conjugated Polymers

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Abstract: Reaction of 2 equivs of MesC≡CPh with $Cp_2Zr(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$(pyr) afforded the zirconacyclopentadiene $Cp_2Zr[2,5\text{-}Ph_2\text{-}3,4\text{-}Mes_2C_4]$. The regiochemistry of this isomer ($\beta\beta$ with respect to the mesityl substituents) was determined through single-crystal X-ray analysis and 2D (NOESY, HSQC, HMBC) NMR experiments. This selectivity is attributed largely to a steric-based directing effect of the *o*-methyl ring substituents since coupling of 1,3-dimethyl-2-(phenylethynyl)benzene with zirconocene gave a single regioisomer (*o*-xylyl groups in both β-positions) while coupling of 1,3-dimethyl-5-(phenylethynl)benzene gave a statistical distribution of zirconacyclopentadiene regioisomers. The coupling reaction of 2 equivs of MeC≡CMes or PrC≡CMes with $Cp_2Zr(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$(pyr) at ambient temperature gave the $\beta\beta$ regioisomers, $Cp_2Zr[2,5\text{-}Me_2\text{-}3,4\text{-}Mes_2C_4]$ and $Cp_2Zr[2,5\text{-}Pr_2\text{-}3,4\text{-}Mes_2C_4]$, respectively, as the major products. Heating solutions of these zirconacycles at 80 °C for several hours resulted in an increase in the amount of the unsymmetrical product. For reaction mixtures of PrC≡CMes and $Cp_2Zr(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$(pyr) the major (and apparently thermodynamic) product under these reaction conditions was $Cp_2Zr[2,4\text{-}Mes_2\text{-}3,5\text{-}Pr_2C_4]$. The steric strain in the mesityl-substituted zirconacycles allowed for facile substitution reactions of MesC≡CPh or PrC≡CMes by less bulky alkynes (i.e., tolan and 3-hexyne) to give the unsymmetrical ziconacyclopentadienes $Cp_2Zr[2,4,5\text{-}Ph_3\text{-}3\text{-}MesC_4]$, $Cp_2Zr[2\text{-}Ph\text{-}3\text{-}Mes\text{-}4,5\text{-}Et_2C_4]$, and $Cp_2Zr[2\text{-}Pr\text{-}3\text{-}Mes\text{-}4,5\text{-}Ph_2C_4]$. Reaction of a mesityl-terminated diyne containing a rigid dihexylfluorenylene spacer with zirconocene afforded poly(*p*-fluorenylenedienylene) after demetalation with benzoic acid.

Introduction

The reductive coupling of alkynes by zirconocene is an important carbon−carbon bond forming reaction.[1−3] The resulting zirconacyclopentadienes are useful precursors to a wide range of organic molecules including (for example) dienes,[4] arenes,[5−12] cyclopentadienes,[13−15] cyclopentadienones,[16] thiophenes,[17,18] phospholes,[19] thiophene oxides,[20] and bicyclic compounds[21] via electrophilic substitution of the metal center. When unsymmetrical alkynes are coupled, an important factor that determines the structure of the product is the regiochemistry for the alkyne coupling at zirconium, which is known to be sensitive to both steric and electronic factors. In general, sterically demanding groups such as $-SiMe_3$ and $-CMe_3$ direct alkyne couplings such that they adopt the less-crowded 2- and 5- (α) positions of the zirconacyclopentadiene ring.[21−23] In addition to promoting regioselectivity, sterically demanding alkyne substituents also promote reversibility for alkyne

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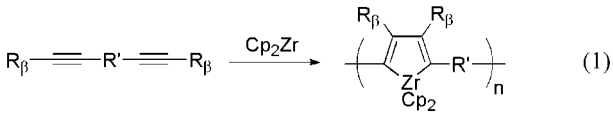
couplings and give labile metallacycles.[24,25] On the other hand, electron-poor substituents (e.g., pentafluorophenyl groups) prefer the 3- and 4- (β) positions of the zirconacyclopentadiene ring. This has been explained in terms of charge distributions in the transition state for alkyne coupling, which has a highly unsymmetrical structure according to DFT calculations and is best described as an alkyne adduct of a zirconacyclopropene.[26]

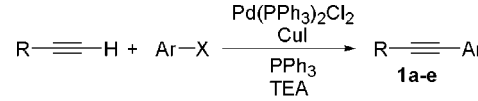
The ability to control the coupling of unsymmetrical alkynes in a regioselective manner is not only useful for the synthesis of small molecules but also for the synthesis of macrocycles[27−33] and polymers[26,34] via the coupling of diynes of the type RC≡C−R′−C≡CR containing a rigid spacer group (R′). For the synthesis of macrocycles by this method, another important requirement is that the alkyne substituents promote reversibility for zirconacyclopentadiene formation.[27] Thus, $-SiMe_3$-terminated diynes are well suited for macrocycle synthesis, since the silyl group preferentially adopts the α-position of the metallocyclic ring and enhances the reversibility required for supramolecular assembly of the macrocycles. Although a variety of macrocycles have been synthesized by varying the size and geometry of the spacer group R′, this approach has so far been limited to diynes terminated with $-SiMe_3$. Unfortunately, zirconacyclopentadienes with $-SiMe_3$ substituents are difficult to convert to corresponding aromatic or heterocyclic derivatives, presumably because of the formidable steric barrier presented by the silyl groups.[35] Thus, it is of interest to develop alternative, more synthetically versatile macrocyclization strategies. This might be accomplished with smaller α-directing groups and/or β-directing groups that induce reversibility for the alkyne coupling. The identification of new β-directing groups (R_β) would also enable regioselective syntheses of conjugated oligomers and polymers, with conjugated R′ spacer groups directed to the α-positions (eq 1).[26]



(1)

In an attempt to further develop new methodologies for the control of regioselectivity and reversibility in the coupling of alkynes by zirconocene, the synthesis of zirconacyclopentadienes from mesityl-terminated alkynes was examined. The mesityl (Mes) group is relatively bulky, and this property was expected to provide regioselective couplings. As described herein, mesityl groups kinetically prefer to couple into the β-positions of zirconacyclopentadiene rings. Interestingly, this β-directing group is electronically distinct from the other β-director that has been identified (the $-C_6F_5$ group).[26] Significantly, mesityl groups have also been found to promote reversibility for such couplings. In this contribution, these properties are shown to provide routes to unsymmetrical zirconacyclopentadienes and regioregular, conjugated polymers.

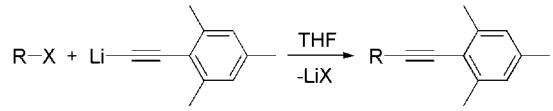
Scheme 1



	R	Ar
a	Ph	Mes
b	Ph	
c	Ph	
d	Ph	
e	4-BuPh	Mes

Results and Discussion

Alkyne Synthesis. The alkynes used in this study were synthesized in moderate to high yields by two methods: Pd/Cu-catalyzed coupling of aryl halides with terminal acetylenes (Scheme 1) or nucleophilic substitution of alkyl halides with lithium(mesityl) acetylide (eq 2). It was observed that heating the reaction mixtures (triethylamine solutions) to reflux was required for the Pd/Cu promoted cross-coupling reactions to occur. In order to keep the catalytic palladium species stable at these elevated temperatures 4 equivs of PPh_3 per equiv of palladium were required. Terminal alkynes with low boiling points (i.e., propyne and pentyne) were not suitable as reactants for the synthesis of alkynes **1f** and **1g** by this method, but these alkynes proved to be accessible by the nucleophilic substitution route (eq 2).



(2)

1f, R = Me
1g, R = Pr

Zirconocene Coupling of MesC≡CPh. Reaction of 2 equivs of MesC≡CPh (**1a**) with Rosenthal's $Cp_2Zr(pyr)(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$[36] at room temperature afforded the homocoupled zirconacyclopentadiene (eq 3). Similar results were also observed for the coupling of **1a** at low temperature using Negishi's zirconocene synthon.[37] Of the three zirconacyclopentadiene regioisomers possible from the homocoupling of unsymmetrical alkynes (αα-, αβ-, or ββ-positions), the coupling of **1a** exclusively formed one product (by ^1H NMR), and the regiochemistry was determined through X-ray crystallographic structural analysis and 1D and 2D (NOESY, HSQC, HMBC) NMR experiments of the isolated product. The NMR spectra of zirconacycle **2a** are consistent with a symmetric product,

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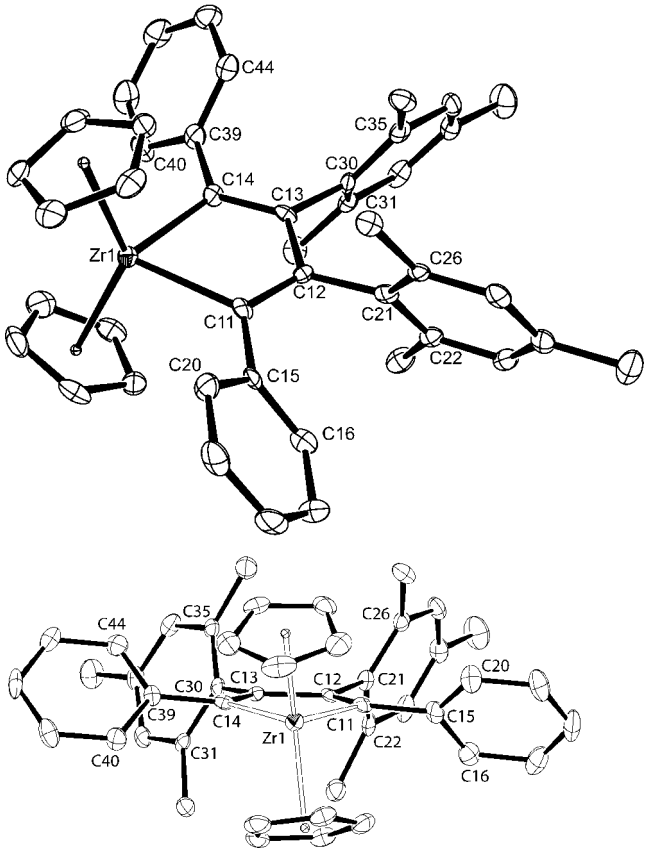
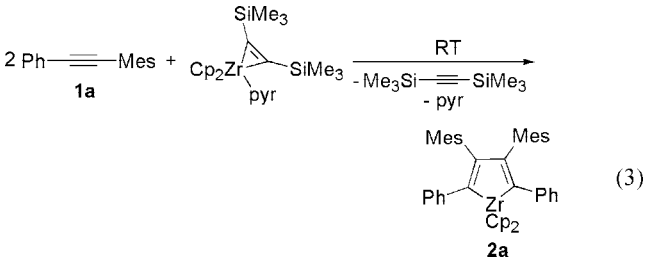


Figure 1. ORTEP depiction of the solid-state molecular structure of **2a** in two different orientations. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn with 50% probabilities. Compound **2a** crystallized in the $P2_1/c$ space group with the following refinement parameters: R1 = 0.040, wR2 = 0.045, and GOF = 1.40. Selected bond lengths (Å), bond angles (deg): Zr1−C11, 2.267(4); Zr1−C14, 2.269(4); C11−C12, 1.369(5); C12−C13, 1.510(5); C13−C14, 1.373(5); Cp_{cent}−Zr1−Cp_{cent}, 135.76(2); C11−Zr1−C14, 77.8(1).

which indicates that the mesityl group prefers to couple exclusively in either the α- or β-position of the zirconacyclopentadiene ring. In the ^{13}C NMR spectra, the most downfield signals are generally indicative of a zirconium-bound sp^2 carbon atom.[38,39] The 2D C−H correlation NMR spectrum (HMBC, optimized for 2−3 bond coupling) of zirconacycle **2a** exhibits cross peaks between the *ortho* protons of the phenyl ring (6.53 ppm) and the most downfield carbon resonance (196.3 ppm) which indicates that the mesityl group preferentially couples into the β-position of the zirconacyclopentadiene ring. X-ray structural analysis conclusively established the molecular structure, and the ORTEP diagram[40] is shown in Figure 1.



(3)

Zirconacyclopentadiene **2a** crystallizes with one molecule and 1 equiv of toluene in the asymmetric unit. The zirconacyclopentadiene framework is essentially planar. All four aryl substituents of the zirconacyclopentadiene are tilted in a propeller-like arrangement such that each molecule is chiral; however, the crystal structure is not chiral. The phenyl rings are twisted less than the mesityl rings with respect to the zirconacyclopentadiene plane. The mesityl rings exhibit torsion angles of 110.9(4)° (C11−C12−C21−C22) and 109.3(4)° (C12−C13−C30−C31) with respect to the butadiene backbone, while the phenyl rings display related torsion angles of 135.1(4)° (C12−C11−C15−C20) and 140.1(4)° (C13−C14−C39−C40). This propeller-like arrangement also influences the positions of the Cp rings about zirconium, such that the Cp_{cent}−Zr1−Cp_{cent} plane is tilted by 6.8° away from perpendicularity with the C11−Zr1−C14 plane. Presumably, this "twisting" of the molecule results from steric pressures propagated by the mesityl groups.

It seemed that these sterically encumbered zirconacyclopentadienes might fragment to release free alkyne in a manner similar to that of zirconacyclopentadienes containing the −$SiMe_3$ group.[24] If such a fragmentation process were reversible, an equilibrium between the different possible regioisomers might be established. To address the possibility that **2a** is not the thermodynamic product of the coupling of **1a**, this zirconacycle was heated at 110 °C in benzene-d_6 and the solution was monitored by ^1H NMR spectroscopy over the course of 48 h. During this time, there was no observable change in the resulting spectrum. As shown below, these conditions lead to ring fragmentation and alkyne substitution. Thus, the observed regioisomer from the coupling of **1a** by zirconocene appears to be the thermodynamic and kinetic product of the reaction.

Influence of Other Methyl-Substituted Aryl Groups on Alkyne Coupling. To understand the factors that cause the mesityl group to preferentially couple into the β-position of the zirconacyclopentadiene ring, zirconocene-mediated couplings of two related alkynes that contain *o*-methyl substituents, 1,3-dimethyl-2-(phenylethynyl)benzene (**1b**) and 1-methyl-2-(phenylethynyl)benzene (**1c**), were investigated (Scheme 2). The reaction of 2 equivs of alkyne **1b** with $Cp_2Zr(pyr)(\eta^2$-$Me_3SiC{\equiv}CSiMe_3)$ at ambient temperature resulted in quantitative conversion to a symmetrical product, and no further changes were observed in the ^1H NMR spectrum, even after heating at 110 °C for 6 h. Large-scale synthesis of zirconacycle **2b** provided an orange powder in 81% yield, and assignment of this complex as the $\beta\beta$ regioisomer was confirmed by 2D (HSQC, HMQC, NOESY) NMR spectroscopy. Thus, it appears that the *p*-methyl substitution in **1a** does not substantially affect the regioselectivity of zirconocene coupling, likely because this group does not exert a steric influence on this reaction.

Despite decreased steric hindrance at the reactive alkyne center, zirconocene coupling of 1-methyl-2-(phenylethynyl)benzene (**1c**) is highly regioselective (Scheme 2). By ^1H NMR spectroscopy, reaction of 2 equivs of alkyne **1c** with $Cp_2Zr(pyr)(\eta^2$-$Me_3SiC{\equiv}CSiMe_3)$ at ambient temperature in benzene-d_6 gave a 66% yield of the symmetrical zirconacyclopentadiene product (**2c**) and the remaining product is identified as the unsymmetrical regioisomer (**3**). The ^1H NMR spectrum is complicated by restricted rotation of the pendant *o*-tolyl groups, and zirconacycle

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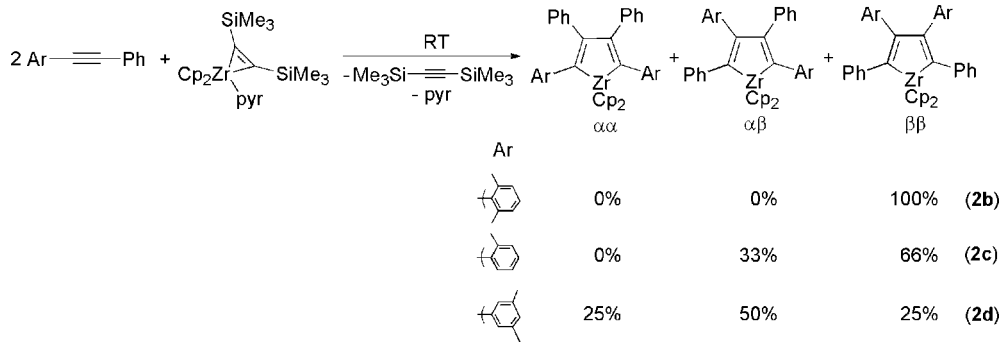
Scheme 2. Observed Regioselectivities for the Zirconocene Couplings of **1b**−**d**[a]



[a] As determined by ^{1}H NMR spectroscopy of the crude reaction mixture.

2c exists as two atropisomers (syn/anti = 2:5). Zirconacycle **3** also exists as two atropisomers but the broadness of the peaks (conversion between atropisomers is on the NMR time scale) prevents accurate integration of the resonances due to overlap. Heating the mixture of symmetrical and unsymmetrical zirconacyclopentadienes at 110 °C for 18 h resulted in a thermodynamic equilibrium between the two regioisomers consisting of 88% of **2c** and 12% of **3**, with no change in the syn/anti ratio of zirconacycle **2c**. Large-scale generation of zirconacycle **2c** was achieved using the Negishi protocol,[37] followed by heating in toluene to ensure a thermodynamic distribution of products.

Unfortunately, the mixture of zirconacyclopentadienes derived from **1c** could not be separated into pure components, so it was demetalated by stirring with benzoic acid, and ^{1}H NMR spectroscopy of the crude butadiene products indicates that the same ratio of regioisomers exists. The minor regioisomer was removed by washing with hexanes and ethanol to give 2,2′-((1*E*,3*E*)-1,4-diphenylbuta-1,3-diene-2,3-diyl)bis(methylbenzene) (**4**) as a white powder in 62% yield. Variable-temperature ^{1}H NMR spectroscopy in benzene-d_6 indicates that **4** exhibits restricted rotation, with a coalescence temperature for the vinyl resonances of 82 °C. Since **4** is a mixture of atropisomers, the absolute regiochemistry could not be determined by 2D NMR spectroscopy. Thus, the structure was determined by single-crystal X-ray diffraction, which indicates that the *o*-tolyl groups occupy the β-positions of the symmetrical zirconacycle **2c** (Figure 2). Butadiene **4** crystallizes exclusively in the anti configuration with the *o*-tolyl groups nearly perpendicular to the planar butadiene backbone (88.6 (3)°). On the other hand, the phenyl groups are in conjugation with the butadiene backbone and twist out of planarity with the butadiene by only 17.3(4)°.

To investigate whether electronic factors play a role in the regioselectivities observed for the formation of zirconacycles **2a**−**c**, zirconocene-mediated coupling of 1,3-dimethyl-5-(phenylethynyl)benzene (**1d**) was examined. The reaction of 2 equivs of alkyne **1d** with 1 equiv of $Cp_2Zr(pyr)(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$ in benzene-d_6 at ambient temperature generated a statistical mixture of αα, αβ, and $\beta\beta$ regioisomers, as determined by ^{1}H NMR spectroscopy, and no further changes were observed upon heating at 110 °C for 6 h. Clearly, the *o*-methyl substituents in **1a**−**c** provide a sterically based directing effect during zirconocene coupling and selectively adopt the β positions of the metallacycle.

Zirconocene Coupling of Additional Mesitylalkynes. To further explore the influence of the substituent effects on the zirconocene couplings of mesitylalkynes, couplings with alkynes **1e**−**g** were examined. Reaction of 2 equivs of the appropriate alkyne with $Cp_2Zr(pyr)(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$ at ambient temperature afforded the homocoupled zirconacyclopentadienes **2e**−**g** in moderate yields (Scheme 3). The regiochemistry of the products was determined by 1D and 2D (NOESY, HSQC, HMBC) NMR experiments and zirconacycle **2g** was also structurally characterized by X-ray crystallography (Figure 3). In all three cases, the mesityl group preferentially adopted the β-position of the zirconacyclopentadiene.

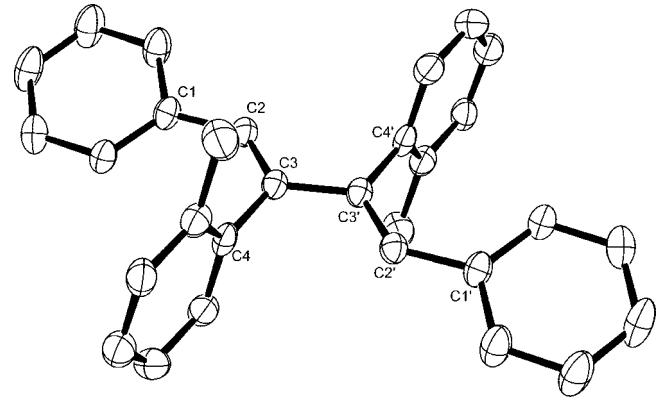
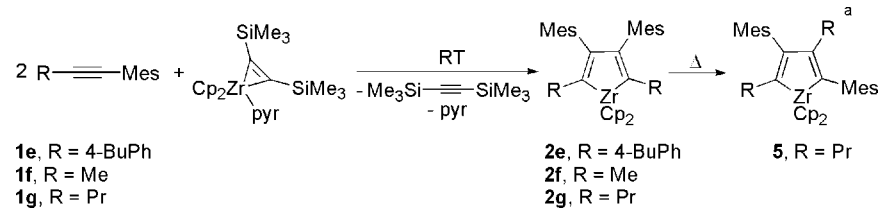


Figure 2. ORTEP depiction of the solid-state molecular structure of **4**. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn with 50% probabilities. Compound **4** crystallized in the $P2_1/n$ space group with the following refinement parameters: R1 = 0.056, wR2 = 0.14, and GOF = 1.17. Selected bond lengths (Å), bond angles (deg): C1−C2, 1.469(4); C2−C3, 1.354(4); C3−C4, 1.495(4); C4−C4′, 1.484(5); C1−C2−C3, 131.1(2).

The crude reaction mixtures were also analyzed by NMR spectroscopy. The coupling of alkyne **1e** with $Cp_2Zr(pyr)(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$ in benzene-d_6 at ambient temperature results in only one product, which is spectroscopically equivalent to isolated zirconacycle **2e**. In contrast, coupling of alkynes **1f** or **1g**, under the same reaction conditions, gave two products. In both cases, the major product (92% yield in both cases) was the isolated, symmetrical zirconacycle (**2f** or **2g**), based on ^{1}H NMR spectroscopy. The crude reaction mixtures were then heated at 80 °C, to allow for zirconacyclopentadiene fragmentation (*vide infra*), and the solutions were monitored by ^{1}H NMR spectroscopy. The reaction mixture involving alkyne **1e** did not exhibit any change in the NMR spectrum after 24 h at this elevated temperature. However, heating the reaction mixtures of **1f** and **1g** resulted in an increase in the amount of the minor (unsymmetrical) product. Heating the reaction mixture of alkyne **1f** with $Cp_2Zr(pyr)(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$ for 24 h resulted in an increase in the amount of minor product to 33%. This

Scheme 3[a]



1e, R = 4-BuPh
1f, R = Me
1g, R = Pr

2e, R = 4-BuPh
2f, R = Me
2g, R = Pr

5, R = Pr

[a] This product was not observed when R = 4-BuPh.

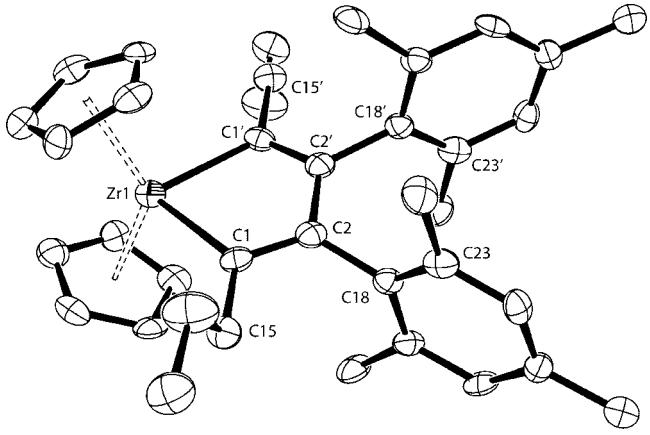


Figure 3. ORTEP depiction of the solid-state molecular structure of **2g**. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn with 50% probabilities. Compound **2g** crystallized in the *Pnna* space group with the following refinement parameters: R1 = 0.037, wR2 = 0.064, and GOF = 0.71. Selected bond lengths (Å), bond angles (deg): Zr1−C1, 2.254(5); C1−C2, 1.370(6); C2−C2′, 1.498(8); C1−C15, 1.501(6); C2−C18, 1.516(6); Cp_{cent}−Zr1−Cp_{cent}, 132.7; C1−Zr1−C1′, 82.1(3).

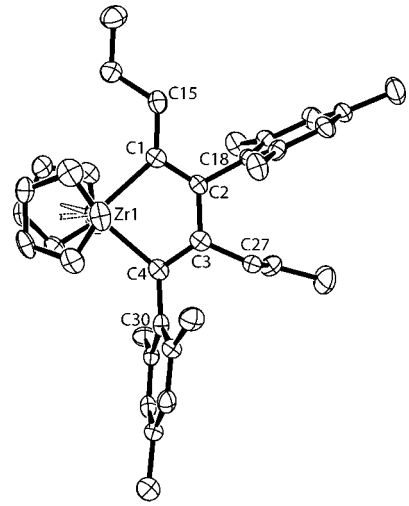


Figure 4. ORTEP depiction of the solid-state molecular structure of **5**. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn with 50% probabilities. Compound **5** crystallized in the $P\bar{1}$ space group with the following refinement parameters: R1 = 0.056, wR2 = 0.115, and GOF = 0.97. Selected bond lengths (Å), bond angles (deg): Zr1−C1, 2.232(5); Zr1−C4, 2.269(5); C1−C2, 1.347(7); C2−C3, 1.503(7); C3−C4, 1.363(6); Cp_{cent}−Zr1−Cp_{cent}, 130.6; C1−Zr1−C4, 83.4(2).

unsymmetrical zirconacycle exhibits a ^{1}H NMR resonance for the Cp ligand at 5.99 ppm, and two Me resonances for the terminal Me groups of 1.49 and 1.30 ppm. The reaction mixture involving **1g** was heated at 80 °C for 24 h to result in a complete reversal in product distribution, such that the unsymmetrical zirconacycle **5** formed in a 90% yield (by ^{1}H NMR spectroscopy). Since the unsymmetrical product is the major (and thermodynamic) product under these conditions, it could be isolated and fully characterized. The molecular structure, determined by X-ray crystallography, is shown in Figure 4.

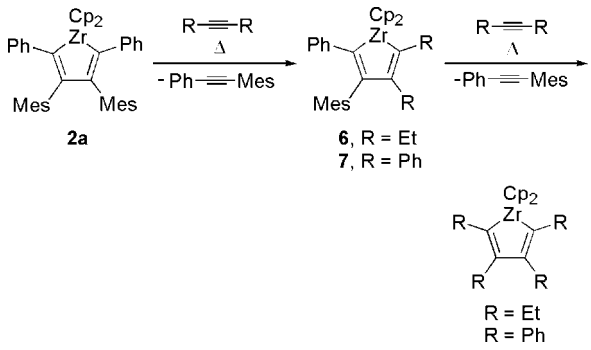
This difference in reactivity between (alkyl)C≡CMes and (aryl)C≡CMes indicates that the steric bulk of the group opposite the mesityl group is also important in determining regioselectivity. The mesityl group of PrC≡CMes may be accommodated into the α-position of a zirconacyclopentadiene without significant steric interactions, as indicated by the formation of zirconacycle **5**. If PhC≡CMes (**1a**) were to couple with its mesityl group in the α-position, the propeller-like geometry of the mesityl and phenyl rings about the zirconacycle would cause steric interactions between the methyl groups of the α-mesityl substituent and the Cp ligands. The α-mesityl group of zirconacycle **5** avoids this interaction by adopting a geometry that is nearly perpendicular to the zirconacyclopentadiene backbone (*vide infra*).

Although zirconacycles **2a** and **2g** possess mesityl groups in both β-positions, there are significant differences between the two structures. While compound **2a** has a nearly planar zirconacyclopentadiene framework, the zirconacycle ring of **2g** is puckered such that C2 (and C2′) lies out of the C1−Zr−C1′ plane by 0.102 Å. The mesityl rings of **2g** exhibit torsion angles of 93.4(6)° (C1−C2−C18-C23) with respect to the butadiene backbone (vs 110.9(4)° and 109.3(4)° for zirconacycle **2a**). The distortion of the zirconacyclopentadiene backbone of **2g** is apparently due to the near perpendicularity of the mesityl rings with respect to the metallocycle, and avoidance of methyl−methyl contacts involving these substituents. Unlike **2a**, which has phenyl groups in the α-positions and can adopt a propeller-like geometry, **2g** has α-propyl groups which occupy a significant volume between the Cp ligands and the mesityl groups according to space-filling models. The mesityl−mesityl interaction of **2g** results in displacements of these groups "up and down" with respect to the plane of the zirconacyclopentadiene framework, to give a C18−C2−C2′−C18′ torsion angle of 25.7°.

The structure of the unsymmetrical zirconacycle **5** is relatively unremarkable. As for **2a**, the zirconacyclopentadiene framework is nearly planar. With the propyl groups occupying the 3- and 5-positions of the metallacyclic ring, the two mesityl rings are tilted toward each other and exhibit torsion angles with respect to the zirconacyclopentadiene ring of 84.9(6)° (mesityl group in the α-position) and 92.1(6)° (mesityl group in the β-position). There is a small deviation from perpendicularity of the Cp_{cent}−Zr1−Cp_{cent} plane relative to the C1−Zr1−C4 plane, of 2.0°.

Reversibility of Zirconocene Couplings. The strain in the structure of zirconacycle **2a**, as demonstrated by the "twisting" of the molecule (*vide supra*), and the thermodynamic equilibrium between the regioisomers from the coupling of **1c**, suggested that the zirconocene coupling of **1a** might be readily reversible. This is further supported by the observation of

exchange reactions of alkyne moieties in **2a** with 3-hexyne and tolan at elevated temperatures. Zirconacycle **2a** was combined with 2.1 equivs of 3-hexyne in benzene-d_6 at 85 °C. After 24 h, ^{1}H NMR spectroscopy indicated quantitative monosubstitution to give the unsymmetric zirconacycle **6** (eq 4). The regiochemistry of **6**, with the mesityl group in the β-position, was established by 2D NMR (COSY, NOESY, HSQC, HMBC) spectroscopy. Gas chromatography−mass spectrometry of the protonolysis product ($M^+ = 304$) was also consistent with quantitative monosubstitution. Although heating at 110 °C for 36 h did not result in further substitution of PhCCMes moiety in **6**, increasing the temperature to 150 °C and heating for 72 h afforded 2,3,4,5-tetraethylzirconacyclopentadiene in quantitative yield (on the basis of ^{1}H NMR spectroscopy).

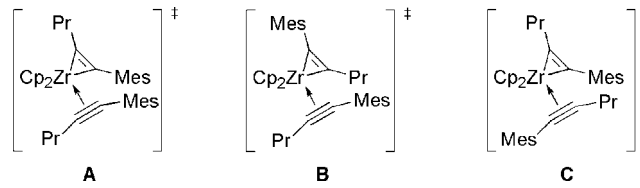


(4)

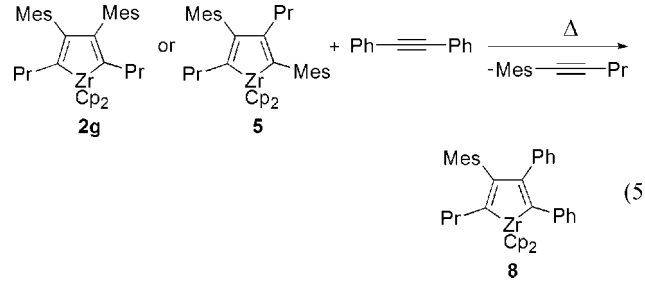
Substitution reactions of **2a** with 2.1 equiv of tolan follow a similar sequence of events. After heating at 85 °C for 24 h, ^{1}H NMR spectroscopy indicates quantitative monosubstitution to give 3-mesityl-2,4,5-triphenylzirconacyclopentadiene (**7**), and the regiochemistry of this product was again determined by 2D NMR (COSY, NOESY, HSQC, HMBC) spectroscopy. The identification of this product was corroborated by gas chromatography−mass spectrometry of the protonolysis product ($M^+ = 400$). In addition, 64% conversion to 2,3,4,5-tetraphenylzirconacyclopentadiene was achieved upon heating at 110 °C for 36 h, and 93% conversion was observed after 5 days.

To examine the substitution of a MesCCPr moiety in $Cp_2Zr[2,5\text{-}Pr_2\text{-}3,4\text{-}Mes_2C_4]$ (**2g**), this compound was heated at 60 °C in the presence of 1 equiv of tolan for 24 h. Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy indicates that all of the starting zirconacycle was consumed and two new products with Cp resonances at 6.10 and 6.00 ppm are observed in 74% and 26% yield, respectively. The minor product was identified as tetraphenylzirconacyclopentadiene on the basis of its ^{1}H NMR shifts. The major product was isolated by crystallization from pentane and characterized as the unsymmetrical zirconacycle $Cp_2Zr[2\text{-}Pr\text{-}3\text{-}Mes\text{-}4,5\text{-}Ph_2C_4]$ (**8**) in 47% yield (eq 5). The regiochemistry of the product was determined by 2D (COSY, NOESY, HSQC, HMBC) NMR spectroscopy. Similarly, $Cp_2Zr[2,4\text{-}Mes_2\text{-}3,5\text{-}Pr_2C_4]$ (**5**) was allowed to react with 1 equiv of tolan at 100 °C for 14 h in benzene-d_6 and the crude reaction mixture was analyzed by ^{1}H NMR spectroscopy. Qualitatively, the results are the same in that substitution of the MesCCPr moiety results in the unsymmetrical zirconacycle **8** and the fully substituted tetraphenylzirconacyclopentadiene. These two products formed in a 1:1 ratio after all the tolan was consumed, and some of the starting zirconacycle **5** remained. This may be due to the elevated temperature required for alkyne substitution in **5**. Although this type of reversible coupling has been observed with $-SiMe_3$- and $-CMe_3$-substituted alkynes, it is often difficult to selectively substitute a single alkyne

Scheme 4



bearing these substituents from a symmetrical zirconacyclopentadiene.[23] In contrast, substitution reactions of mesityl-substituted alkynes readily afford the monosubstituted, unsymmetrical zirconacyclopentadiene product.



(5)

It is interesting to consider the influence of the mesityl group on the above isomerization and substitution reactions from a mechanistic perspective. The initial reaction steps of zirconocene alkyne coupling (and decoupling) involve the formation of a transient 16-electron zirconacyclopropene.[41,42] Subsequently, a second equivalent of alkyne rapidly inserts into the transient zirconacyclopropene to form the observed zirconacyclopentadiene product. The transition state of this insertion has been shown to closely resemble an alkyne adduct of a zirconacyclopropene and does not contain two equally activated, metal-bound alkynes.[26,43] For the coupling of (aryl)C≡CMes, formation of a symmetrical zirconacycle, in which both mesityl groups are in the β-positions of the zirconacyclopentadiene ring, occurs under kinetic and thermodynamic conditions. The β,β-dimesityl(zirconacyclopentadiene) is also the major product under kinetic conditions for the coupling of (alkyl)C≡CMes. This indicates that the lowest energy transition states generally have both mesityl groups oriented away from the metal center (Scheme 4, **A**). For the coupling of (alkyl)C≡CMes under thermodynamic conditions there are two possible transition states to consider (Scheme 4, **B** and **C**). Unfortunately, it was not possible to experimentally distinguish between the two transition states. In addition, for the above substitution reactions, the mesityl group preferentially couples into the β-position of the resulting zirconacyclopentadiene ring and this indicates that having two mesityl groups in the system may be important for such a group to couple into the α-position.

Zirconocene-Coupling Routes to Polymers. Preliminary investigations indicate that the regioselective zirconocene coupling of mesitylalkynes may be useful in the syntheses of mesityl-substituted oligomers and polymers via the coupling of diynes of the type MesC≡C−R′−C≡CMes containing a rigid spacer group (R′). Significantly, the substituent opposite the mesityl

(41) Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1989**, *111*, 2870–2874.
(42) Miller, A. D.; McBee, J. L.; Tilley, T. D. *J. Am. Chem. Soc.* **2008**, *130*, 4992–4999.
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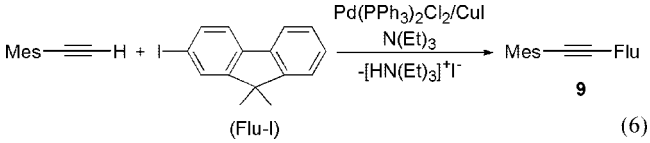
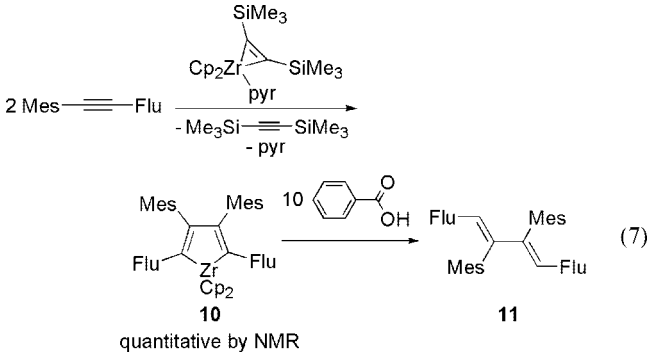
group on the alkyne has a considerable influence on the regiochemical outcome of alkyne coupling (*vide supra*). Since (aryl)C≡CMes substrates appear to give highly regioselective couplings, diynes containing aryl spacer groups appear to be well suited to this approach. In particular, fluorenylene groups appear to be attractive since they may be readily derivatized to influence solubility properties, and conjugated fluorene-containing polymers have proven to be promising electromluminescent materials with good thermal and oxidative stability.[44−48] With this in mind, a simple, model coupling reaction involving a fluorenyl-substituted alkyne was targeted.

The alkyne 9,9-dimethyl-2-(mesitylethynyl)fluorene (**9**) was synthesized by a procedure similar to that used for the synthesis of alkynes **1a**−**e** (eq 6). The zirconocene coupling of alkyne **9** using either the Negishi protocol or $Cp_2Zr(pyr)(\eta^2$-$Me_3SiC{\equiv}CSiMe_3)$ gave the same symmetrical zirconacycle and the regiochemistry was determined by 2D (COSY, NOESY, HSQC, HMBC) NMR spectroscopy. Coupling with $Cp_2Zr(pyr)(\eta^2$-$Me_3SiC{\equiv}CSiMe_3)$ was rather slow at room temperature and heating at 80 °C for 12 h allowed for the substitution of both the $Me_3SiC{\equiv}CSiMe_3$ and pyridine ligands to give zirconacycle **10** in high yield. Thus, the couplings of alkynes substituted with mesityl and fluorenyl groups are expected to proceed with high regioselectivity.



(6)

It was also of interest to determine which metal-transfer reactions might be appropriate for post-polymerization modification of the resulting zirconium-containing polymer. It has been observed that the efficiency of the metal-transfer reactions of zirconocene are influenced by substituents in both the α- and β-positions of the zirconacycle.[28,49,50] Reactions of zirconacycle **10** with either sulfur monochloride or sulfur dioxide led to a mixture of products and were too low-yielding to be useful for post-polymerization modifications. On the other hand, demetalation of zirconacycle **10** with an excess of benzoic acid gave butadiene **11** in 97% isolated yield (eq 7).



(7)

The diyne to be used in the polymerization was synthesized analogously to alkyne **9**, and the solubility properties were enhanced by incorporation of hexyl groups into the fluorenylene spacer (eq 8). Diyne **12** was coupled with $Cp_2Zr(pyr)(\eta^2$-$Me_3SiC{\equiv}CSiMe_3)$, and the reaction mixture was heated at 80 °C for 16 h to afford the zirconium-containing polymer. This was subsequently demetalated in the same reaction flask to produce the bright yellow polymer **13** in 80% yield (eq 9). The

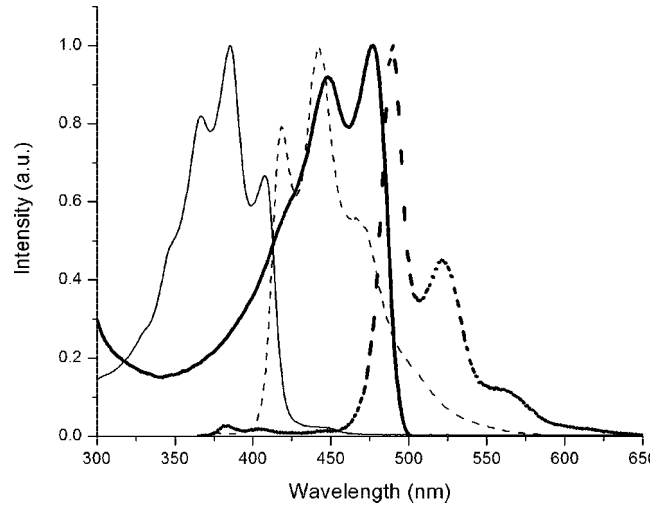
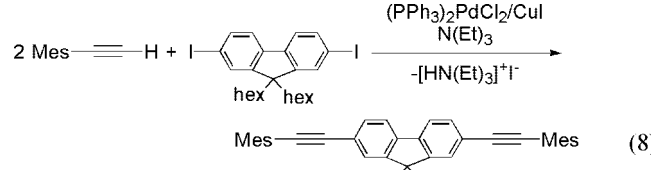
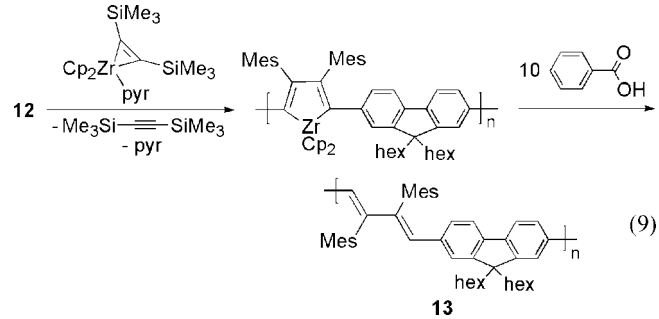


Figure 5. UV−vis and photoluminescent (PL) spectra of model compound **11** (UV−vis, thin solid line; PL, thin dashed line) and polymer **13** (UV−vis, bold solid line; PL, bold dashed line).

^{1}H NMR spectrum of **13** is consistent with that of butadiene **11** and the infrared spectrum is noticeably absent of absorptions due to C≡C bonds (2100−2260 cm^{-1}), although it cannot be stated with certainty that the polymer is completely regioregular. The number-average molecular weight of this polymer (M_n = 24 400; by gel permeation chromatography with polystyrene standards) is significantly higher than corresponding values for previously synthesized regioregular, conjugated polymers obtained by the zirconocene coupling of diynes.[26] This is most likely due to the high solubility in common organic solvents (i.e., THF and toluene) afforded by the substituted fluorenylene spacer. The UV−vis and fluorescence spectra of polymer **13** were obtained and compared to those of the model compound, butadiene **11** (Figure 5). The λ_{max} of polymer **13** is red-shifted significantly compared to the λ_{max} value of compound **11**, and this demonstrates the increase in conjugation length for the polymerized species (477 vs 385 nm).



(8)



(9)

Concluding Remarks

The coupling of mesityl-substituted alkynes by zirconocene provides new methodologies for the control of regioselectivity

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and reversibility in this important carbon−carbon bond forming reaction. Significantly, the mesityl group exhibits a kinetic preference for coupling into the β position of the zirconacyclopentadiene derivative, and enhances zirconacycle fragmentation. This observed regioselectivity is in contrast to that observed for $-SiMe_3$- and $-CMe_3$-substituted alkynes which preferentially couple into the α position of the resulting zirconacyclopentadiene. Furthermore, alkyne substitutions in β,β-dimesityl-substituted zirconacyclopentadienes appears to proceed in a stepwise manner such that the first alkyne substitution (especially of MesC≡C(aryl)) is more facile. This should enable a number of selective transformations to unsymmetrical zirconacyclopentadienes that may prove synthetically useful. As an illustration of the utility of mesityl-terminated alkynes in a regioselective coupling reaction, the conjugated poly(*p*-fluorenylenedienylene) **13** was prepared. Especially given the high selectivity exhibited by couplings of (aryl)C≡CMes derivatives, a number of potentially useful conjugated polymers may be obtained by related zirconocene couplings of mesityl-terminated diynes. Other potential applications include oligomer and macrocycle syntheses that utilize the regioselectivity and the reversibility afforded by the mesityl substituent.[51]

Interestingly, the regioselectivities observed for (aryl)C≡CMes and (alkyl)C≡CMes alkynes are somewhat different. While the kinetic and (apparently) thermodynamic products of (aryl)C≡CMes coupling are the same (the $\beta\beta$ regioisomer), the coupling of (alkyl)C≡CMes kinetically produces the $\beta\beta$ regioisomer which then isomerizes at elevated temperature (ca. 80 °C) to the $\alpha\beta$ regioisomer as the major product. In contrast, the aryl-substituted zirconacycle was observed to be stable at 110 °C over 2 days and no change in the regiochemistry of the substituents was observed. While this difference between aryl- and alkyl-substituted alkynes is not completely understood, the X-ray structures indicate the kinetic product of the coupling of PrC≡CMes (the $\beta\beta$ regioisomer) is more sterically congested. In this isomer, the adjacent mesityl groups are significantly canted with respect to one another and exhibit a relatively large torsion angle of 25.7° (C18−C2−C2′−C18′). On the other hand, the $\alpha\beta$ regioisomer has a nearly planar zirconacyclopentadiene framework that exhibits a torsion angle with respect to the β substituents of 0.3° (C18−C2−C3−C27). Presumably, steric constraints in the transition state for alkyne−alkyne coupling strongly favor a positioning of both mesityl groups into the β positions. However, the combination of *n*-propyl and mesityl groups results in different steric interactions about the zirconacyclopentadiene ring, such that the $\alpha\beta$ regioisomer is more thermodynamically stable.

Experimental Section

General Procedures. Unless noted, all manipulations were performed under a dry, nitrogen atmosphere using either standard Schlenk techniques or a nitrogen-filled glovebox. Dry, oxygen-free solvents were used. Olefin impurities were removed from pentane by treatment with concentrated H_2SO_4, 0.5 N $KMnO_4$ in 3 M H_2SO_4, and saturated $NaHCO_3$. Pentane was then dried over $MgSO_4$, stored over activated 4 Å molecular sieves, and distilled from potassium benzophenone ketyl under a nitrogen atmosphere. Toluene was purified by stirring with concentrated H_2SO_4, washing with saturated $NaHCO_3$, and then drying over $CaCl_2$ and distillation from sodium under a nitrogen atmosphere. Spectrophotometric grade diethyl ether and reagent grade THF were distilled from sodium benzophenone ketyl under a nitrogen atmosphere. Acetonitrile was refluxed over P_2O_5 and distilled under a nitrogen atmosphere. Benzene-d_6 was vacuum distilled over sodium/potassium alloy and benzophenone.

NMR spectra were recorded on a Bruker AVB-400 instrument operating at 400.1 (^{1}H) and 100.7 MHz (^{13}C) with a Bruker AV-300 instrument operating at 300.1 MHz (^{1}H), or with a Bruker DRX-500 instrument operating at 500.1 (^{1}H) and 125.8 MHz (^{13}C). Chemical shifts are reported in ppm relative to $SiMe_4$ and are referenced internally to residual solvent resonances (^{1}H, ^{13}C). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet. Elemental analyses were performed by the Microanalytical Laboratory in the College of Chemistry at the University of California, Berkeley. 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.

The compounds $Cp_2Zr(pyr)(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$,[36] mesitylacetylene,[52] 9,9-dimethyl-2-iodofluorene,[53] and 9,9-dihexyl-2,7-diiodofluorene[48] were synthesized according to published procedures. All other chemicals were obtained from commercial suppliers and used as received. The *n*-butyl lithium was used as 1.6 or 2.5 M solutions in hexanes.

Phenylethynylmesitylene (1a). The cuprous iodide (0.21 g, 1.1 mmol) and tetrakis(triphenylphosphine)palladium (0.65 g, 0.56 mmol) were loaded into a Teflon-sealed flask. Mesityl iodide (2.77 g, 11.3 mmol) and phenylacetylene (1.24 mL, 11.3 mmol) were loaded into a separate flask and dissolved in triethylamine (40 mL). This solution was then cannula-transferred into the flask containing the catalysts, the solution was briefly degassed under vacuum, and the flask was sealed. The reaction mixture was heated at 80 °C for 1 h. The crude product was purified by column chromatography (pentane) to give a white solid in 81% yield (2.00 g, 9.1 mmol), which was identified spectroscopically.[54] ^{1}H NMR (400 MHz, C_6D_6): δ 7.50 (m, 2H), 7.02 (m, 3H), 6.73 (s, 2H), 2.49 (s, 6H), 2.08 (s, 3H). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ 140.3, 137.8, 131.7, 128.6, 128.1, 126.5, 124.6, 120.6, 97.7, 88.2, 21.3, 21.2.

1,3-Dimethyl-2-(phenylethynyl)benzene (1b). A flask was loaded with dichlorobis(triphenylphosphine)palladium(II) (75 mg, 0.1 mmol), CuI (41 mg, 0.2 mmol), and triphenylphosphine (56 mg, 0.2 mmol). A degassed mixture of triethylamine (25 mL) and 2-iodo-1,3-dimethylbenzene (1.00 g, 4.3 mmol) was transferred via cannula into the flask containing the solids. Phenylacetylene (0.58 mL, 5.3 mmol) was added and the reaction was stirred under reflux for 16 h. The resulting suspension was diluted with diethyl ether (50 mL) and was washed successively with a saturated, aqueous solution of NH_4Cl (2 × 50 mL), water (50 mL), and brine (50 mL). The organic layer was collected, dried over anhydrous $MgSO_4$, filtered, and concentrated. Column chromatography (silica gel, hexanes) afforded a white solid in 74% yield (0.66 g, 3.2 mmol), which was identified spectroscopically.[55] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (m, 2H), 7.38 (m, 3H), 7.11 (m, 3H), 2.54 (s, 6H).

1-Methyl-2-(phenylethynyl)benzene (1c). See the synthesis of **1b** for the general procedure. The reagents used were $(PPh_3)_2PdCl_2$

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(54) Bosch, E.; Hubig, S. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1998**, *120*, 386–395.
(55) Cao, D.; Schollmeyer, D.; Meier, H. *Eur. J. Org. Chem.* **1999**, *79*, 1–795.

(75 mg, 0.1 mmol), CuI (41 mg, 0.2 mmol), PPh_3 (56 mg, 0.2 mmol), 1-iodo-2-methylbenzene (1.00 g, 4.6 mmol), and phenylacetylene (0.61 mL, 5.6 mmol). Purification by column chromatography (silica gel, hexanes) afforded a clear, colorless liquid in 81% yield (0.71 g, 3.7 mmol), which was identified spectroscopically.[56] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 (m, 3H), 7.35 (m, 3H), 7.22 (m, 3H), 2.51 (s, 3H).

1,3-Dimethyl-5-(phenylethynyl)benzene (1d). See the synthesis of **1b** for the general procedure. The reagents used were $(PPh_3)_2PdCl_2$ (75 mg, 0.1 mmol), CuI (41 mg, 0.2 mmol), PPh_3 (56 mg, 0.2 mmol), 1-iodo-3,5-dimethylbenzene (1.00 g, 4.3 mmol), and phenylacetylene (0.58 mL, 5.3 mmol). Purification by column chromatography (silica gel, hexanes) afforded a yellow oil in 93% yield (0.83 g, 4.0 mmol), which was identified spectroscopically.[54] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (m, 2H), 7.35 (m, 3H), 7.18 (s, 2H), 6.99 (s, 1H), 2.30 (s, 6H).

(4-Butylphenyl)ethynylmesitylene (1e). The mesityl iodide (0.50 g, 2.0 mmol), CuI (0.010 g, 0.053 mmol), $(PPh_3)_2PdCl_2$ (40 mg, 0.057 mmol), and PPh_3 (0.028 g, 0.11 mmol) were loaded into a flask and to this was added triethylamine (25 mL). To the resulting solution was added the 1-butyl-4-ethynylbenzne (0.40 mL, 2.2 mmol) and the reaction flask was equipped with a reflux condenser. The reaction mixture was heated at reflux for 40 h. The reaction was quenched with saturated, aqueous solution of NH_4Cl (25 mL) and then filtered through a plug of silica gel and rinsed with hexanes. The reaction mixture was then collected and washed with a saturated, aqueous solution of NH_4Cl (40 mL), dilute HCl (40 mL), water (40 mL), and brine (40 mL). The organic layer was collected, dried with $MgSO_4$, filtered, concentrated, and purified by column chromatography (hexanes) to give a clear oil in 63% yield (0.35 g, 1.2 mmol). ^{1}H NMR (500 MHz, C_6D_6): δ 7.54 (m, 2H), 6.95 (d, $^3J_{H-H}$ = 8.0 Hz, 2H), 6.76 (s, 2H), 2.54 (s, 6H), 2.39 (t, $^3J_{H-H}$ = 7.8 Hz, 2H), 2.10 (s, 3H), 1.43 (m, 2H), 1.20 (tq, $^3J_{H-H}$ = 7.5 Hz, 2H), 0.85 (t, $^3J_{H-H}$ = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ 143.4, 140.6, 138.0, 132.1, 129.2, 128.5, 122.3, 121.2, 98.4, 87.9, 36.2, 34.0, 22.9, 21.7, 21.6, 14.5. GC-MS: m/z = 276 (M^+). Anal. Calcd for $C_{21}H_{24}$: C, 91.25; H, 8.75. Found: C, 91.50; H, 8.61.

Mesityl-1-propyne (1f). The mesitylacetylene (1.00 g, 6.9 mmol) was dissolved in 50 mL of THF. The solution was cooled to −78 °C in a dry ice/isopropanol bath, and BuLi (4.4 mL, 6.9 mmol) was added dropwise. After 10 min the cold bath was removed and the solution was stirred at ambient temperature for 2 h. The mesitylacetylide solution was then cooled to −78 °C and methyl iodide (0.43 mL, 6.9 mmol) was added dropwise via syringe. After 10 min the cold bath was removed and the solution was stirred at ambient temperature for 4 h. The solvent was removed, and the resulting oil was dissolved in diethyl ether (100 mL). This solution was then washed with a saturated, aqueous solution of $NaHCO_3$ (100 mL), water (100 mL), an aqueous solution of 2 N NaOH (100 mL), and brine (100 mL). The organic layer was collected, dried with $MgSO_4$, and concentrated. The residue was purified by flash chromatography (hexanes) to yield a clear oil that solidified upon standing (80%, 0.85 g, 5.4 mmol), which was characterized spectroscopically.[57] ^{1}H NMR (500 MHz, C_6D_6): δ 6.74 (s, 2H), 2.48 (s, 6H), 2.09 (s, 3H), 1.78 (s, 3H).

Mesityl-1-pentyne (1g). The mesitylacetylene (1.00 g, 6.9 mmol) was dissolved in 50 mL of THF. The solution was cooled to −78 °C in a dry ice/isopropanol bath and BuLi (4.4 mL, 6.9 mmol) was added dropwise. After 10 min the cold bath was removed and the solution was stirred at ambient temperature for 2 h. The propyl bromide (0.63 mL, 6.9 mmol) was added dropwise via syringe and the reaction mixture was heated at 60 °C for 48 h. The solvent was then removed, and the resulting oil was dissolved in diethyl ether (100 mL). This solution was washed with a saturated, aqueous solution of $NaHCO_3$ (100 mL), water (100 mL), an aqueous solution of 2 N NaOH (100 mL), and brine (100 mL). The organic layer was collected, dried with $MgSO_4$, and concentrated. The residue was purified by flash chromatography (hexanes) to yield a light yellow oil (62%, 0.80 g, 4.3 mmol). ^{1}H NMR (500 MHz, C_6D_6): δ 6.74 (s, 2H), 2.50 (s, 6H), 2.28 (t, $^3J_{H-H}$ = 6.8 Hz, 2H), 2.10 (s, 3H), 1.48 (tq, $^3J_{H-H}$ = 7.0 Hz, 2H), 0.95 (t, $^3J_{H-H}$ = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ 140.4, 137.1, 128.3, 121.9, 98.3, 79.7, 23.2, 22.3, 21.7, 21.6, 14.0. GC-MS: m/z = 186 (M^+). Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 89.87; H, 9.78.

$Cp_2Zr[2,5\text{-}Ph_2\text{-}3,4\text{-}Mes_2C_4]$ (2a). The Cp_2ZrCl_2 (0.29 g, 0.98 mmol) was loaded in a flask, dissolved in hexanes (5 mL) and THF (20 mL), and the resulting solution was cooled to −78 °C. To this solution was added BuLi (1.23 mL, 2.0 mmol) dropwise via syringe. This solution was allowed to react for 5 min before the phenylethynylmesitylene (**1a**) (0.43 g, 2.0 mmol) in hexanes (20 mL) was added via syringe. The reaction mixture was allowed to warm to room temperature over 1 h and was then allowed to react for 12 h. The solvent was removed, and the resulting solid was washed with hexanes (40 mL) to give an orange solid in 90% yield (0.59 g, 0.88 mmol). X-ray quality crystals were grown from a concentrated toluene solution at −30 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 6.98 (t, $^3J_{H-H}$ = 7.3 Hz, 4H), 6.75 (t, $^3J_{H-H}$ = 7.3 Hz, 2H), 6.53 (d, $^3J_{H-H}$ = 7.3 Hz, 4H), 6.48 (s, 4H), 6.09 (s, 10H), 2.33 (s, 12H), 1.88 (s, 6H). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ 196.3 (−Zr*C*(Ph)═C(Mes)−), 147.6 (*i*-Ph), 146.1 (−ZrC(Ph)═*C*(Mes)−), 138.1 (*i*-Mes), 136.8 (*o*-Mes), 134.8 (*p*-Mes), 128.4 (*m*-Ph), 127.9 (*m*-Mes), 126.8 (*o*-Ph), 123.6 (*p*-Ph), 111.8 (Cp), 22.6 (*o*-Me), 20.9 (*p*-Me). Anal. Calcd for $C_{44}H_{42}Zr$: C, 79.83; H, 6.37. Found: C, 79.55; H, 6.15.

Alternative Procedure for $Cp_2Zr[2,5\text{-}Ph_2\text{-}3,4\text{-}Mes_2C_4]$ (2a). In a glovebox, $Cp_2Zr(pyr)(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$ (0.67 g, 1.42 mmol) and alkyne **1a** (0.63 g, 2.84 mmol) were loaded into a flask. Benzene (15 mL) was transferred via cannula onto the solids, and the reaction mixture was stirred at ambient temperature for 18 h. The solvent was removed under vacuum, and the crude product was washed with pentane (2 × 30 mL) to give a red powder in 84% yield (0.79 g, 1.2 mmol).

$Cp_2Zr[2,5\text{-}Ph_2\text{-}3,4\text{-}o\text{-}Xyl_2C_4]$ (2b). The alternative procedure for **2a** was repeated with 1,3-dimethyl-2-(phenylethynyl)benzene (**1d**) (0.40 g, 1.94 mmol) to give an orange solid in 81% yield (0.50 g, 0.79 mmol). ^{1}H NMR (400 MHz, C_6D_6): δ 6.98 (m, 4 H), 6.77 (m, 4 H), 6.67 (d, J = 7 Hz, 4 H), 6.52 (d, J = 7 Hz, 4 H), 6.09 (s, 10 H), 2.31 (s, 12 H); ^{13}C NMR (100 MHz, C_6D_6): δ 196.5 (−Zr*C*(Ph)═C(Xyl)−), 147.9 (*i*-Ph), 146.0 (−ZrC(Ph)═*C*(Xyl)−), 141.1 (*i*-Xyl), 137.4 (*o*-Xyl), 128.3 (*m*-Ph), 127.20 (*o*-Ph), 127.19 (*m*-Xyl), 126.4 (*p*-Xyl), 124.1 (*p*-Xyl), 112.2 (Cp), 23.1 (Me). Anal. Calcd for $C_{42}H_{38}Zr$: C, 79.57; H, 6.04. Found: C, 79.60; H, 6.25.

$Cp_2Zr[2,5\text{-}(4\text{-}BuPh)_2\text{-}3,4\text{-}Mes_2C_4]$ (2e). 1e (0.22 g, 0.80 mmol) and $Cp_2Zr(pyr)(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$ (0.19 g, 0.40 mmol) were loaded into separate flasks. To the flask containing the (4-butylphenyl)ethynylmesitylene was added toluene (20 mL) and this solution was cannula-transferred to the flask containing $Cp_2Zr(pyr)(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$. The reaction mixture was stirred at room temperature for 16 h. The solvent was then removed and the resulting solid was washed with pentane (2 × 5 mL) to give a red solid in 33% yield (0.10 g, 0.13 mmol). ^{1}H NMR (500 MHz, C_6D_6): δ 6.87 (d, $^3J_{H-H}$ = 8.0 Hz, 4H), 6.52 (m, 8H), 6.18 (s, 10H), 2.38 (s, 12H), 2.36 (t, $^3J_{H-H}$ = 7.8 Hz, 4H), 1.90 (s, 6H), 1.40 (m, 4H), 1.18 (tq, $^3J_{H-H}$ = 7.5 Hz, 4H), 0.80 (t, $^3J_{H-H}$ = 7.5 Hz, 6H). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ 196.6 (−Zr*C*(4-BuPh)═C(Mes)−), 146.4 (−ZrC(4-BuPh)═*C*(Mes)−), 145.4 (*i*-4-BuPh), 138.7 (*i*-Mes), 138.1 (*p*-4-BuPh), 137.2 (*o*-Mes), 135.0 (*p*-Mes), 128.30 (*m*-4-BuPh), 128.28 (*m*-Mes), 127.2 (*o*-4-BuPh), 112.1 (Cp), 35.8 (Bu), 34.0 (Bu), 23.07 (Bu), 23.05 (*o*-Me), 21.3 (*p*-Me), 14.5 (Bu). Anal. Calcd for $C_{52}H_{58}Zr$: C, 80.67; H, 7.55. Found: C, 80.83; H, 7.62.

$Cp_2Zr[2,5\text{-}Me_2\text{-}3,4\text{-}Mes_2C_4]$ (2f). 1f (0.50 g, 3.2 mmol) and $Cp_2Zr(pyr)(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$ (0.74 g, 1.6 mmol) were loaded

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into a flask and then dissolved in toluene (30 mL). The reaction mixture was stirred at room temperature for 16 h. The solvent was removed, and the resulting solid was washed with pentane (10 mL) and diethyl ether (20 mL) to give an orange solid in 50% yield (0.43 g, 0.80 mmol). ^{1}H NMR (400 MHz, C_6D_6): δ 6.68 (s, Mes, 4H), 6.11 (s, Cp, 10H), 2.38 (s, *o*-Me, 12 H), 1.99 (s, *p*-Me, 6H), 1.35 (s, α-Me, 6H). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ 187.2 (−Zr*C*(Me)═C(Mes)−), 142.7 (−ZrC(Me)═*C*(Mes)−), 139.0 (*i*-Mes), 136.5 (*o*-Mes), 134.7 (*p*-Mes), 128.4 (*m*-Mes), 111.0 (Cp), 22.2 (α-Me), 22.0 (*o*-Me), 21.3 (*p*-Me). Anal. Calcd for $C_{34}H_{38}Zr$: C, 75.92; H, 7.12. Found: C, 75.57; H, 7.21.

$Cp_2Zr[2,5\text{-}Pr_2\text{-}3,4\text{-}Mes_2C_4]$ (2g). 1g (0.20 g, 1.1 mmol) and $Cp_2Zr(pyr)(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$ (0.25 g, 0.55 mmol) were loaded into separate flasks. To the flask containing $Cp_2Zr(pyr)(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$ was added 10 mL of toluene, and to the flask containing the alkyne was added 5 mL of toluene. The alkyne solution was then added to the zirconocene solution via cannula transfer. The reaction mixture was stirred at room temperature for 16 h. The solvent was removed, the resulting solid was dissolved in pentane (50 mL), and this solution was then cannula filtered to remove residual solids. The pentane solution was concentrated to saturation (20 mL) and the resulting solution was cooled to −30 °C for 16 h. The solvent was then removed by cannula filtration to give orange crystals in 58% yield (0.14 g, 0.23 mmol). ^{1}H NMR (300 MHz, C_6D_6): δ 6.64 (s, 4H), 6.18 (s, 10H), 2.36 (s, 12H), 1.94 (m, 10H), 1.06 (m, 4H), 0.74 (t, $^3J_{H-H}$ = 7.2 Hz, 6H). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ 193.3 (−Zr*C*(Pr)═C(Mes)−), 139.9 (*i*-Mes), 139.3 (−ZrC(Pr)═*C*(Mes)−), 136.3 (*o*-Mes), 134.7 (*p*-Mes), 128.4 (*m*-Mes), 110.9 (Cp), 42.2 (Pr), 24.9 (Pr), 22.6 (*o*-Me), 21.3 (*p*-Me), 15.8 (Pr). Anal. Calcd for $C_{38}H_{46}Zr$: C, 76.84; H, 7.81. Found: C, 76.95; H, 7.88.

2,2′-((1*E*,3*E*)-1,4-diphenylbuta-1,3-diene-2,3-diyl)bis(methylbenzene) (4). A solution of Cp_2ZrCl_2 (0.42 g, 1.42 mmol) in THF (15 mL) was cooled to −78 °C, BuLi (1.77 mL, 2.84 mmol) was added, and the mixture was stirred for 15 min. A solution of alkyne **1c** (0.60 g, 3.12 mmol) in THF (15 mL) was added, and the resulting reaction mixture was slowly warmed to ambient temperature over 2 h, followed by stirring for an additional 12 h. After removal of the solvent under vacuum, crude zirconacycle **2c** was extracted with toluene (25 mL), and the resulting solution was stirred at 110 °C for 48 h. Demetalation was achieved by cooling to ambient temperature, adding benzoic acid (0.52 g, 4.26 mmol), and stirring for 16 h. The reaction was quenched with water (50 mL) and washed successively with a saturated, aqueous solution of $NaHCO_3$ (50 mL), water (50 mL), and brine (50 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated to a pale yellow solid. Washing with hexanes (2 × 20 mL) and ethanol (2 × 20 mL) gave a white powder in 62% yield (0.34 g, 0.88 mmol). X-ray quality crystals were grown by slow evaporation of a concentrated acetone solution. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29−7.37 (m, 6 H), 7.21−7.26 (m, 2 H), 7.01−7.06 (m, 6 H), 6.65−6.70 (m, 4 H), 6.19 (s, 1 H), 6.18 (s, 1 H), 2.27 (s, 3 H), 2.26 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.40, 143.35, 138.9, 138.8, 137.18, 137.15, 136.8, 136.6, 130.66, 130.57, 130.44, 130.38, 130.28, 130.0, 129.0, 127.9, 127.70, 127.67, 126.75, 126.72, 126.63, 126.56, 19.6, 19.3; two peaks were obscured by overlap with solvent. GC-MS: m/z = 386 (M^+). Anal. Calcd for $C_{30}H_{26}$: C, 93.22; H, 6.78. Found: C, 92.94; H, 6.74.

$Cp_2Zr[2,4\text{-}Mes_2\text{-}3,5\text{-}Pr_2C_4]$ (5). 1g (0.20 g, 1.1 mmol) and $Cp_2Zr(pyr)(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$ (0.25 g, 0.55 mmol) were loaded into separate flasks. To the flask containing $Cp_2Zr(pyr)(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$ was added 10 mL of toluene, and to the flask containing the alkyne was added 5 mL of toluene. The alkyne solution was then added to the zirconocene solution via cannula transfer. The reaction mixture was stirred at 80 °C for 16 h. The solvent was removed, the resulting solid was dissolved in pentane (40 mL), and this solution was then cannula-filtered to remove residual solids. The pentane solution was concentrated to saturation (15 mL), and the resulting solution was cooled to 0 °C for 4 h. The supernatant was then removed by cannula filtration to give orange crystals in 19% yield (0.060 g, 0.10 mmol). ^{1}H NMR (300 MHz, C_6D_6): δ 6.92 (s, 2H), 6.89 (s, 2H), 6.06 (s, 10H), 2.58 (s, 6H), 2.39 (s, 6H), 2.23 (s, 3H), 2.19 (s, 3H), 1.97 (m, 2H), 1.71 (m, 2H), 1.12 (m, 4H), 0.71 (t, $^3J_{H-H}$ = 7.4 Hz, 3H), 0.42 (t, $^3J_{H-H}$ = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ 195.0 (−Zr*C*(Pr)═C(Mes)−), 189.1 (−Zr*C*(Mes)═C(Pr)−), 146.9 (α-*i*-Mes), 140.5 (β-*i*-Mes), 139.6 (−ZrC(Mes)═*C*(Pr)−), 136.9 (−ZrC(Pr)═*C*(Mes)−), 135.8 (β-*o*-Mes), 135.3 (β-*p*-Mes), 132.4 (α-*p*-Mes), 131.9 (α-*o*-Mes), 129.6 (α-*m*-Mes), 128.7 (β-*m*-Mes), 111.7 (Cp), 42.5 (α-Pr), 36.7 (β-Pr), 24.0, (α-Pr), 23.0 (β-Pr), 22.2 (α-*o*-Me), 21.6 (α-*p*-Me), 21.3 (β-*o*-Me), 21.2 (β-*p*-Me), 16.0 (α-Pr), 15.6 (β-Pr). Anal. Calcd for $C_{38}H_{46}Zr$: C, 76.84; H, 7.81. Found: C, 76.47; H, 7.79.

$Cp_2Zr[2\text{-}Ph\text{-}3\text{-}Mes\text{-}4,5\text{-}Et_2C_4]$ (6). Zirconacycle **2a** (10 mg, 15 μmol) and 3-hexyne (4 μL, 36 μmol) were dissolved in benzene-d_6 (ca. 500 mg) and loaded into a Teflon-sealed NMR tube. The tube was placed in an 85 °C oil bath and monitored by ^{1}H NMR spectroscopy at regular intervals over 24 h. The solution was then concentrated on vacuum line, to remove excess 3-hexyne, and the regiochemistry was determined by 2D (COSY, NOESY, HSQC, HMBC) NMR spectroscopy. To this NMR tube was then added 3-hexyne (3 μL, 24 μmol), and the tube was placed in a 110 °C oil bath and monitored by ^{1}H NMR spectroscopy at regular intervals over 36 h but minimal change was observed. The tube was then placed in a 150 °C oil bath and monitored by ^{1}H NMR spectroscopy at regular intervals over 72 h. ^{1}H NMR (500 MHz, C_6D_6): δ 7.04 (m, 2H), 6.75 (t, J = 9 Hz, 1H), 6.70 (s, 2H), 6.66 (d, J = 7.5 Hz, 2H), 6.02 (s, 10H), 2.33 (q, J = 8 Hz, 2H), 2.32 (s, 6H), 2.09 (s, 3H), 1.99 (s, J = 8 Hz, 2H), 0.86 (t, J = 8 Hz, 3H), 0.81 (t, J = 8 Hz, 3H). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ 195.9 (−Zr*C*(Et)═C(Et)−), 188.6 (−Zr*C*(Ph)═C(Mes)−), 149.0 (*i*-Ph), 139.0 (*i*-Mes), 138.9 (−ZrC(Et)═*C*(Et)−), 138.7 (−ZrC(Ph)═*C*(Mes)−), 136.3 (*o*-Mes), 135.2 (*p*-Mes), 128.5 (*m*-Mes), 128.3 (*m*-Ph), 126.4 (*o*-Ph), 123.7 (*p*-Ph), 111.3 (Cp), 30.1 (Et), 22.7 (Et), 21.6 (Me), 21.5 (Me), 16.4 (Et), 14.2 (Et).

$Cp_2Zr[2,4,5\text{-}Ph_3\text{-}3\text{-}MesC_4]$ (7). Zirconacycle **2a** (10 mg, 15 μmol) and tolan (6 mg, 34 μmol) were dissolved in benzene-d_6 (ca. 500 mg) and loaded into a Teflon-sealed NMR tube. The tube was placed in an 85 °C oil bath and monitored by ^{1}H NMR spectroscopy at regular intervals over 24 h. The solution was then concentrated on vacuum line and the regiochemistry was determined by 2D (COSY, NOESY, HSQC, HMBC) NMR spectroscopy. The NMR tube was then placed in a 110 °C oil bath and monitored by ^{1}H NMR spectroscopy at regular intervals over 5 days. ^{1}H NMR (500 MHz, C_6D_6): δ 7.02 (m, 4H), 6.93 (d, J = 7.0 Hz, 2H), 6.80 (m, 4H), 6.70 (t, J = 7.2 Hz, 1H), 6.66 (d, J = 7.0 Hz, 2H), 6.62 (d, J = 7.0 Hz, 2H), 6.52 (s, 2H), 6.05 (s, 10H), 2.38 (s, 6H), 1.92 (s, 3H). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ 195.6 (−Zr*C*(Ph)═C(Ph)−), 193.5 (−Zr*C*(Ph)═C(Mes)−), 148.7 (*i*-Ph), 148.3 (*i*-Ph), 144.1 (−ZrC(Ph)═*C*(Ph)−), 142.2 (−ZrC(Ph)═*C*(Mes)−), 141.4 (*i*-Ph), 139.2 (*i*-Mes), 135.9 (*o*-Mes), 135.2 (*p*-Mes), 130.9 (*o*-Ph), 128.7 (*m*-Mes), 128.5 (*m*-Ph), 128.3 (*m*-Ph), 128.0 (*o*-Ph), 127.0 (*m*-Ph), 126.9 (*o*-Ph), 125.6 (*p*-Ph), 124.2 (*p*-Ph), 123.6 (*p*-Ph), 112.4 (Cp), 21.9 (Me), 21.4 (Me).

$Cp_2Zr[2\text{-}Pr\text{-}3\text{-}Mes\text{-}4,5\text{-}Ph_2C_4]$ (8). Zirconacycle **2g** (0.15 g, 0.25 mmol) and tolan (0.045 g, 0.25 mmol) were loaded into a flask and dissolved in toluene (5 mL). The reaction mixture was heated at 60 °C for 30 h, and then the solvent was removed. The crude reaction mixture was dissolved in pentane (10 mL) and then concentrated to saturation. The solution was cooled to −30 °C for 8 h and then the solvent was removed via cannula filtration to give an orange solid in 47% yield (0.070 g, 0.12 mmol). ^{1}H NMR (500 MHz, C_6D_6): δ 7.02 (t, $^3J_{H-H}$ = 7.8 Hz, 2H), 6.90 (d, $^3J_{H-H}$ = 8.0 Hz, 2H), 6.79 (t, $^3J_{H-H}$ = 7.8 Hz, 2H), 6.74 (m, 3H), 6.68 (s, 2H), 6.64 (t, $^3J_{H-H}$ = 7.2 Hz, 1H), 6.10 (s, 10H), 2.38 (s, 6H), 2.09 (m, 2H), 2.01 (s, 3H), 1.03 (m, 2H), 0.74 (t, $^3J_{H-H}$ = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ 195.6 (−Zr*C*(Pr)═C(Mes)−), 191.8 (−Zr*C*(Ph)═C(Ph)−), 149.3 (α-*i*-Ph), 142.4 (β-*i*-Ph), 140.6

(−ZrC(Ph)=*C*(Ph)−), 140.3 (*i*-Mes), 138.7 (−ZrC(Pr)=*C*(Mes)−), 135.3 (*o*-Mes), 135.0 (*p*-Mes), 130.3 (*β*-*o*-Ph), 128.7 (*m*-Mes), 128.5 (α-*m*-Ph), 127.4 (α-*o*-Ph), 126.8 (*β*-*m*-Ph), 125.5 (*β*-*p*-Ph), 123.3 (α-*p*-Ph), 111.7 (Cp), 42.9 (Pr), 25.2 (Pr), 21.42 (*p*-Me), 21.38 (*o*-Me), 16.0 (Pr). Anal. Calcd for $C_{38}H_{38}Zr$: C, 77.89; H, 6.54. Found: C, 77.74; H, 6.32.

9,9-Dimethyl-2-(mesitylethynyl)fluorine (9). The 9,9-dimethyl-2-iodofluorene (0.21 g, 0.66 mmol), CuI (0.010 g, 0.053 mmol), and $(PPh_3)_2PdCl_2$ (40 mg, 0.057 mmol) were loaded into a dry, 20 mL Schlenk flask which was then cooled to −78 °C. A solution of mesitylacetylene in triethylamine was added to the flask under a flow of nitrogen and then triethylamine was added until the total volume in the flask was 15 mL. The cold bath was then removed and the reaction mixture was stirred at room temperature under an atmosphere of nitrogen for 16 h. The reaction was quenched with 15 mL of a saturated, aqueous solution of NH_4Cl and then filtered through a plug of silica gel and rinsed with hexanes. The crude reaction solution was collected and washed with a saturated, aqueous solution of NH_4Cl (30 mL), dilute HCl (30 mL), water (30 mL), and brine (30 mL). The organic layer was dried with $MgSO_4$, filtered, concentrated, and purified by column chromatography (silica gel, hexanes) to give a white solid in 67% yield (0.15 g, 0.44 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (m, 2H), 7.58 (s, 1H), 7.53 (dd, J = 8.0, 1.0 Hz, 1H), 7.45 (m, 1H), 7.34 (m, 2H), 6.92 (s, 2H), 2.53 (s, 6H), 2.32 (s, 3H), 1.53 (s, 6H). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ 154.6, 154.5, 140.7, 140.0, 139.4, 138.2, 131.5, 128.5, 128.3, 127.8, 126.4, 123.6, 123.3, 121.2, 121.0, 120.8, 99.1, 88.7, 47.3, 27.3, 21.71, 21.70. GC-MS: m/z = 336 (M^+). Anal. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19. Found: C, 92.65; H, 7.07.

3,4-Dimesityl-2,5-bis(9,9-dimethylfluoren-2-yl)zirconacyclopentadiene (10). The Cp_2ZrCl_2 (0.22 g, 0.75 mmol) and **9** (0.50 g, 1.5 mmol) were loaded into separate flasks, and to each flask was added THF (10 mL). The flask containing the Cp_2ZrCl_2 solution was cooled to −78 °C, and to this was added a BuLi solution (0.60 mL, 1.5 mmol) dropwise. The reaction mixture was stirred for 1 h, and then the alkyne solution was added by cannula transfer. The reaction mixture was allowed to gradually reach ambient temperature over the next 16 h. The solvent was removed under vacuum, and the resulting solid was dissolved in toluene (20 mL). This solution was cannula-filtered to remove solids. The solvent was then removed under vacuum. The resulting solid was washed with diethyl ether (2 × 20 mL) to give a brick red solid in 60% yield (0.40 g, 0.45 mmol). ^{1}H NMR (500 MHz, C_6D_6): δ 7.57 (d, J = 7.5 Hz, 2H), 7.40 (d, J = 8 Hz, 2H), 7.21−7.16 (m, overlaps residual solvent peak), 6.64 (s, 2H), 6.49 (s, 4H), 6.35 (d, J = 7.5 Hz, 2H), 6.23 (s, 10H), 2.38 (s, 12H), 1.88 (s, 6 H), 1.22 (s, 12H). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ 197.5 (−Zr*C*(Flu)=C(Mes)−), 154.2 (Flu), 153.9 (Flu), 147.4 (−ZrC(Flu)=*C*(Mes)−), 147.1 (Flu), 140.5 (Flu), 138.9 (Mes), 137.4 (Mes), 135.4 (Mes), 135.3 (Flu), 128.3 (Mes), 127.6 (Flu), 127.2 (Flu), 126.7 (Flu), 123.2 (Flu), 121.5 (Flu), 120.1 (Flu), 119.4 (Flu), 112.2 (Cp), 46.9 (Flu), 27.6 (Flu), 23.0 (Mes), 21.2 (Mes). Anal. Calcd for $C_{62}H_{58}Zr$: C, 83.26; H, 6.54. Found: C, 83.14; H, 6.24.

Butadiene 11. Alkyne **9** (0.50 g, 1.5 mmol) and $Cp_2Zr(pyr)(\eta^2$-$Me_3SiC{\equiv}CSiMe_3)$ (0.35 g, 0.74 mmol) were loaded into the same flask and then dissolved in toluene (20 mL). The reaction mixture was then heated at 80 °C for 16 h after which time the flask was removed from heat and allowed to cool to ambient temperature. To the reaction mixture was then added benzoic acid (0.90 g, 7.4 mmol) and the solution was stirred for 16 h. The crude reaction mixture was diluted with toluene (100 mL) and washed successively with a saturated, aqueous solution of $NaHCO_3$ (2 × 100 mL), 2 N NaOH (100 mL), and brine (100 mL). The solvent was removed and the resulting solid was dissolved in hot toluene. This solution was filtered over Celite to remove residual solids and the resulting solution was concentrated to give a bright yellow solid in 97% yield (0.49 g, 0.73 mmol). ^{1}H NMR (500 MHz, C_6D_6): δ 7.44 (m, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.13 (m, 6H), 7.06 (s, 4H), 6.91 (s, 2H), 6.88 (dd, J = 1.6 Hz, J = 8.0 Hz, 2H), 6.83 (s, 2H), 2.45 (s, 12H), 2.34 (s, 6H), 1.14 (s, 12H). ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2): δ 154.6, 153.9, 142.0, 139.4, 138.3, 137.7, 137.4, 137.2, 136.0, 129.60, 129.59, 129.2, 127.6, 127.4, 123.1, 122.8, 120.4, 119.8, 46.9, 27.1, 21.4, 20.7. EI-MS: m/z = 674 (M^+). Anal. Calcd for $C_{52}H_{50}$: C, 92.53; H, 7.47. Found: C, 92.17; H, 7.33.

9,9-Dihexyl-2,7-(dimesitylethynyl)fluorene (12). The 9,9-dihexyl-2,7-diiodofluorene (1.50 g, 2.6 mmol), $(PPh_3)_2PdCl_2$ (36 mg, 0.05 mmol), and CuI (10 mg, 0.05 mmol) were loaded into a round-bottom flask and to this was added triethylamine (30 mL). The mesityl acetylene (0.78 g, 5.4 mmol) was then added to this suspension and the reaction mixture was stirred under nitrogen for 16 h. The reaction mixture was then quenched with a saturated, aqueous solution of NH_4Cl (40 mL) and then filtered through a plug of silica gel and rinsed with hexanes (50 mL). The reaction mixture was then collected and washed with a saturated, aqueous solution of NH_4Cl (40 mL), dilute HCl (40 mL), water (40 mL), and brine (40 mL). The organic layer was collected, dried with $MgSO_4$, filtered, concentrated, and purified by column chromatography (hexanes) to give a yellow solid. The product was further purified by two crystallizations from hexanes at −30 °C to give a pale yellow solid in 33% yield (0.51 g, 0.82 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66 (d, J = 7.8 Hz, 2H), 7.52 (dd, J = 1.2 Hz, J = 7.8 Hz, 2H), 7.46 (s, 2H), 6.92 (s, 4H), 2.53 (s, 12H), 2.31 (s, 6H), 1.99 (m, 4H), 1.10 (m, 12H), 0.77 (t, J = 6.8 Hz, 6H), 0.65 (m, 4H). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 151.3, 140.7, 140.3, 137.9, 130.8, 127.9, 125.7, 122.9, 120.3, 120.1, 98.3, 88.0, 55.4, 40.5, 31.7, 29.9, 23.9, 22.8, 21.6, 21.3, 14.2. IR (NaCl): 2953 s, 2927 s, 2856 s, 2205 w (C≡C), 1480 m (aromatic C=C), 1465 m (aromatic C=C), 1376 w, 1284 w, 1132 w, 1033 w, 888 w, 851 m, 820 m, 726 w cm^{-1}. EI-MS: m/z = 618 (M^+). HRMS Calcd for $C_{47}H_{54}$, 618.4226; Found, 618.4239.

Polymer 13. Diyne **12** (0.26 g, 0.42 mmol) and $Cp_2Zr(pyr)(\eta^2$-$Me_3SiC{\equiv}CSiMe_3)$ (0.20 g, 0.42 mmol) were loaded into the same flask and then dissolved in toluene (12 mL). The reaction mixture was then heated at 80 °C for 16 h after which time the flask was removed from heat and allowed to cool to ambient temperature. To the reaction mixture was added benzoic acid (0.52 g, 4.2 mmol), and the solution was stirred for 16 h. The crude reaction mixture was then concentrated to near saturation and the polymer was purified by precipitation from methanol (300 mL). The resulting solid was collected by filtration and dried under vacuum to give a yellow powder in 80% yield (0.21 g). GPC: M_n/M_w = 24 400/52 950. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.00 (m, 7H), 6.90 (m, 1H), 6.78 (m, 3H), 6.35 (m, 4H), 6.20 (s, 3H), 2.50 (s, 2H), 2.45 (s, 10H), 2.20 (m, 18H), 1.16 (m, 12H), 1.03 (br, 15H), 0.83 (m, 12H). IR (NaCl): 2954 s, 2927 s, 2856 s, 1610 m (aryl-substituted C=C), 1463 s (aromatic C=C), 1377 m, 1355 w, 1261 m, 1095 w, 1033 m, 908 s, 855 m, 814 m, 735 s cm^{-1}. Anal. Calcd for $C_{47}H_{56}$: C, 90.91; H, 9.09. Found: C, 88.57; H, 9.31. (As often observed for conjugated polymers, the combustion analyses typically gave values for the carbon content that were low by a few percent.[4])

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Supporting Information Available: Tables of bond lengths and angles and the X-ray crystallographic data for compounds **2a**, **2g**, **4**, and **5** in the form of CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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