Living Polymerization of Novel Conjugatively Spaced Ferrocenylacetylenes

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ABSTRACT: The synthesis and living metathesis polymerization of five different conjugatively spaced ferrocenylacetylenes, (2-ethynylphenyl)ferrocene **(3)**, (*Z*)-but-1-en-3-ynylferrocene **(4)**, (*E*)-but-1-en-3-ynylferrocene **(5)**, 2-(4-ethynylphen-1-yl)vin-1-ylferrocene **(7)**, and 1-ferrocenyl-2-(4-ethynylphenyl)diazene **(10)** is described. Poly-**10** represents the first polyacetylene containing ferrocenylazoarylene groups. The X-ray structures of two alkynes, **3** and **7**, as well as of one ethynyl precursor, (4-bromophenyl)-ferrocenyldiazene **(8)**, are presented. Polymerizations of all terminal alkynes by the well-defined Schrock metathesis catalysts Mo(N−Ar′)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$ (Ar′ = 2,6-*i*-Pr$_2$C$_6$H$_3$, **11**; Ar′ = 2,6-Me$_2$C$_6$H$_3$, **12**) start solely via β-addition of the corresponding monomer to the initiator except for **3**, which undergoes α-addition with **12**. Presumably due to metathesis-type side reactions, **4** and **5** form only low molecular weight polymers. The polymerizations of **3**, **7**, and **10** proceed in a strongly living manner when either initiator (**11**, **12**) is employed. The polymers are virtually formed via solely head to tail propagation, exhibiting low polydispersities and solubility up to a degree of polymerization (DP) $\approx$ 60. The influence of the spacer on the final properties of the poylmers with regards to their UV−vis absorption spectra and effective conjugation lengths (N_{eff}) is discussed.

Introduction

Fully conjugated polymers based on poly-ynes,[1] poly-enynes,[2] or poly-enes[3] represent interesting materials for many applications in the fields of organic conductivity,[4−8] optoelectronics, and photonics.[9−15] Terminal acetylenes are polymerized preferrably by metathesis polymerization using well-defined Schrock-type metathesis catalysts to yield conjugated poly-enes.[16−25] The degree of conjugation in these materials strongly depends on the electronic as well as steric nature of the substituents in the starting alkyne. The effective conjugation length (N_{eff}) describes the number of coplanar double bonds in a conjugated system. This coplanarity is required for the effective overlap of the p_z-orbitals in the system. Highly conjugated systems show a narrow band gap between HOMO and LUMO that results in low-energy charge-transfer (CT) bands. As a consequence, these materials exhibit strongly bathochromically shifted absorption maxima. The presence of bulky groups in linear polyacetylenes often prevents high values for N_{eff} due to 1,3-steric interactions. Nevertheless, copolymers of alkynes bearing bulky substituents with TCDTF6 (TCDTF6 = 7,8-bis-(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene) may still be highly conjugated.[17] In the course of this copolymerization, the "Feast-momomer"[26] is introduced into the polymer main chain and subsequently converted into three unsubstituted, conjugated double bonds via a thermally induced retro-Diels−Alder reaction. In the case of perfectly alternating copolymers, a sufficient separation of one substituent from the other is achieved. In the case of ferrocene-substituted alkynes, these copolymers sometimes exhibit a remarkable stability due to steric protection by the bulky substituent, despite the large number of unsubstituted double bonds. Unfortunately, the preparation of such perfectly alternating copolymers using ROMP strongly depends on the ratios $k_i(1)/k_p(2)$ and $k_i(2)/k_p(1)$, where $k_i(1)$, $k_i(2)$, $k_p(1)$, and $k_p(2)$ represent the rates of insertion and the rates of propagation of the first and second monomer with the active carbene, respectively. These rate constants cannot be readily controlled, significantly limiting the applicability of this concept.

As a direct consequence, the synthesis of highly conjugated poly-enes via the preparation of homopolymers from a single functional monomer seems highly preferable. For that purpose, the substituted alkyne must fulfill at least two requirements in order to be suitable for synthesis. On one hand, the substituent should possess electron-donating character in order to activate the carbon−carbon triple bond and make it more reactive toward a transition metal alkylidene, which usually speeds up initiation. Additionally, a Lewis-base character provides an enhanced electron density in the resulting polymer backbone. Furthermore, the substitutent should be ideally designed such that the conjugated double bonds in the resulting polyene are as coplanar as possible. This may be achieved by electronic attraction of the substituents (e.g., Π-stacking[27−30]) forcing the backbone into coplanarity.

Acetylenes directly attached to metallocenes have already been polymerized in a living manner.[17] Due to 1,3-interaction, only the "Feast-approach" results in the formation of conjugated materials. In this contribution, we describe the synthesis and living polymerization of

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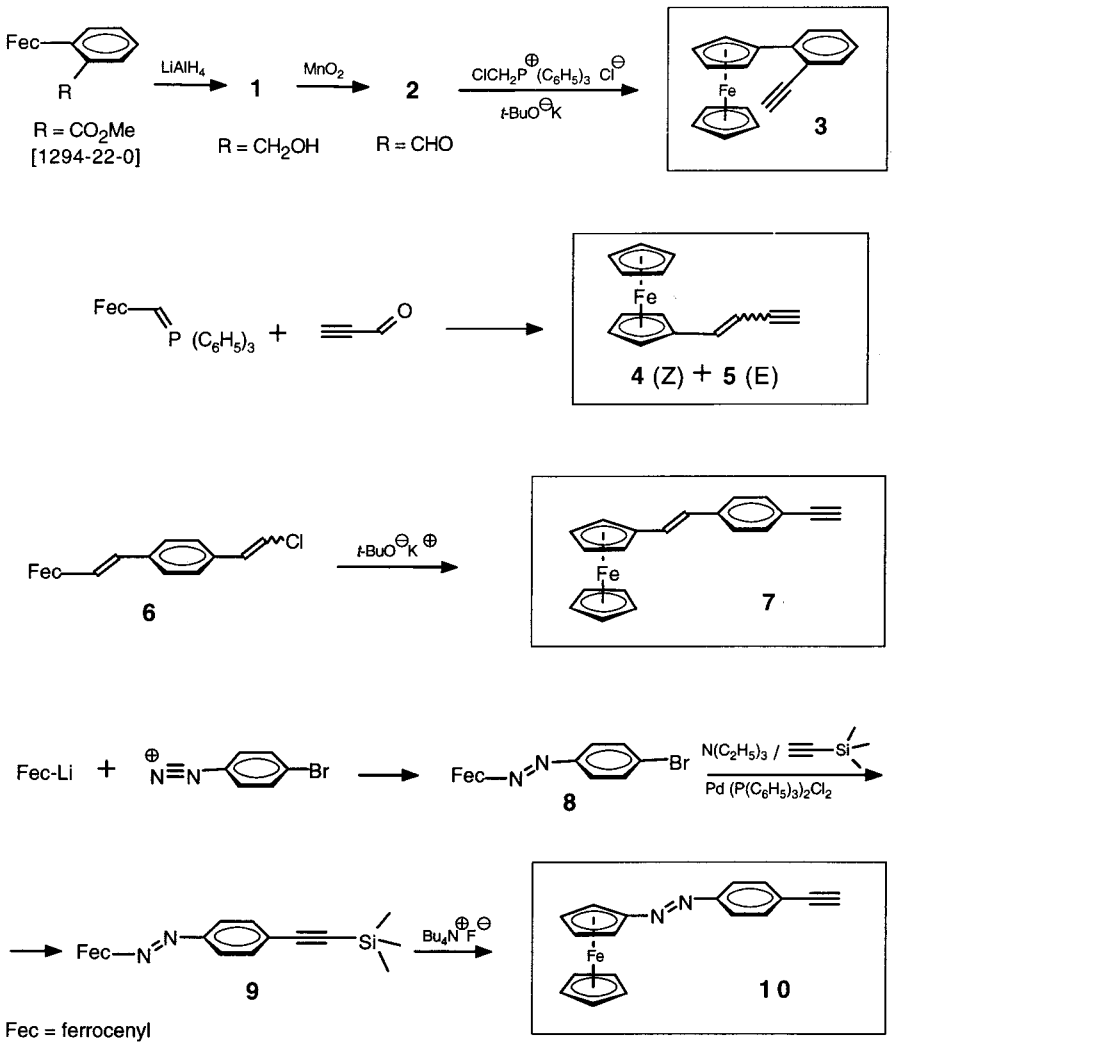
Scheme 1. Reaction Overview for the Preparation of Ethyne Monomers



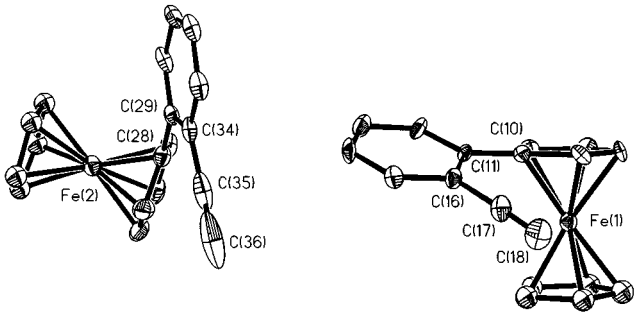


Figure 1. X-ray structure of **3**.

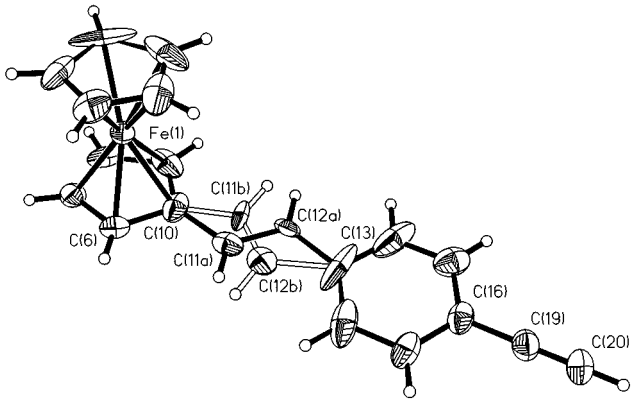


Figure 2. X-ray structutre of **7**.

various ferrocenylacetylenes with conjugated spacers. The length and structure of these spacers has significant influence on the mode of insertion of the alkyne into the Schrock carbene as well as on the structure of the resulting poly-ene.

Results and Discussion

Monomer Synthesis. Five different terminal, ferrocene-substituted acetylenes have been chosen for the present investigation. To contribute to an application-oriented chemistry, they have been synthesized by straightforward synthetic concepts, which allow their preparation in gram quantities. Compounds **3**, **4**, **5**, and **7** were prepared either via Wittig[31−33] or chloro-Wittig[34−36] sequences (Scheme 1). The molecular structures of **3** and **7** are displayed in Figures 1 and 2, respectively. In the asymmetric unit of **3** are two independent molecules, which differ greatly in their conformation. In one, the dihedral angle between the phenyl group and the five-membered ring is found to be 26.6(5)°. As a result, the triple bond points in the direction of the iron atom. The other molecule is twisted in the opposite direction with a dihedral angle of 30.2-(4)°. In contrast to **3**, the dihedral angle of compound **7** between the rings (C6−C10) and (C13−C18) is only 9.5(4)°. Due to this high degree of coplanarity in the solid state, **7** takes advantage of the Lewis base char-

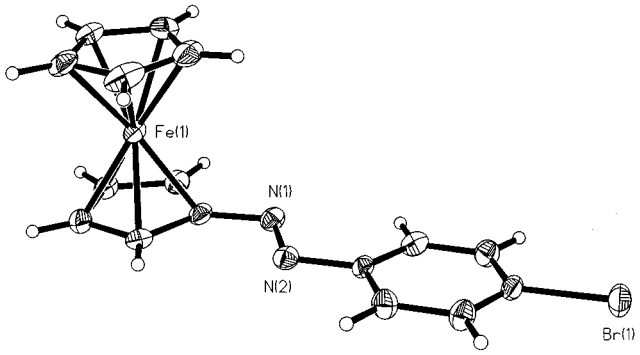


Figure 3. X-ray structure of **8**.

acter of ferrocene. The structure of **7** shows disorder of the double bond C11−C12 in a ratio nearly 1:1. The same disorder has already been described for a similar ferrocenyl compound.[37]

The synthesis of **10** was accomplished via a modified[38] route involving the low-temperature recombination of 4-bromobenzenediazonium tetrafluoroborate[39] with lithioferrocene. This synthetic approach is superior to other procedures,[40−42] as it also allows for the preparation of bromo-substituted arylazoferrocenes, which act as a precursor for trimethylsilyl-protected alkynes via Sonogashira−Hagihara[43] coupling. The corresponding compound, 1-ferrocenyl-2-(4-(2-(trimethylsilyl)ethynyl)-phenyl)diazene (**9**), was prepared in 96% yield. Subsequent deprotection with tetrabutylammonium fluoride yielded **10**. The metathesis polymerization of **10** allows the facile incorporation of a diazene side group into a conjugated polymer. The X-ray structure of the intermediate (*E*)-bromophenyldiazene (**8**), which is a key precursor for **10**, is shown in Figure 3. It reveals the configurational preference of the diaza group for an (*E*)-configuration. The torsion angle between the planes defined by the cyclopentadienyl and the aryl system is only 3.4(3)°. Therefore, this monomer may be considered as almost planar. Compound **10** as well as the precursor **8** represent diazene spacers resistant to photochemical isomerization, which is a favorable feature for NLO conjugates.[44] The high stability of the (*E*)-diazene group stems from the direct substitution with ferrocene, which acts as a photochemical silencer.[45]

Choice of Initiator. To proceed in a living way,[46−48] the polymerization of highly reactive alkynes requires the careful choice of an initiator. For our present investigation, two different initiators were employed. Despite the fact that both of them bear the hexafluoro-*tert*-butoxide ligand, considerable differences in the reactivity toward norbornenes[49] as well as acetylenes had been observed previously.[17] A terminal acetylene is believed to approach an alkylidene initiator at the CNO-face. A way of influencing the mode of insertion was reported by Schrock and co-workers. Their concept of "small-alkoxide" initiators[18,19] in fact favored α-insertion over β-insertion due to steric interactions. Based on previous studies[16,17] as well as on the present contribution, further evidence for the broad applicabilty of this concept is now established. So far, β-insertion was considered to be critical, since it often resulted in the formation of highly reactive, monosubstituted alkylidenes (Figure 4) that interfered with controlled polymerizations.[17] Recently,[16] it was shown that the reaction of sterically demanding and less reactive alkynes with an alkylidene initiator may proceed via β-addition and still be living. Compounds **4**, **5**, **7**, and **10** (Figures 2 and 3) possess a linear structure similar to the previously reported 4-(ferrocenylethynyl)-4′-ethynyltolan.[16] One might therefore be expected to observe β-insertion with both initiators. Due to the high degree of coplanarity and therefore conjugation, the terminal acetylene must be expected to be more active than the one in 4-(ferrocenylethynyl)-4′-ethynyltolan. This should positively influence the polymerization times. As a matter of fact, all compounds investigated except for **3** undergo β-insertion with both initiators (**11**, **12**). For steric reasons, the approach of these monomers toward the CNO face of the initiator is again only possible via β-addition due to the bulky nature of the hexafluoro-*tert*-butoxide moieties. Nevertheless, the active role of the 2,6-substituents of the phenylimido group is clearly evident in the observation that **3** reacts differently with **11** and **12**. While **3** adds β to **11**, it undergoes α-addition with **12**, which may be attributed to its sterically less demanding (2,6-dimethylphenyl)imido group. The ortho-substitution of the phenyl group obviously prevents any steric interaction of the ferrocene substitutent with the hexafluoro-*tert*-butoxide group. This compound therefore behaves similarly to ethynylferrocene, which also reacts by α-addition with **12**.[16] As in the case of ethynylferrocene or ethynylruthenocene, this mode of insertion may additionally be explained by the formation of an electron-rich alkylidene, which compensates for unfavorable sterics. This is accomplished by the Lewis-base properties of ferrocene, which takes advantage of its high conjugation with the phenyl spacer (Figure 1) and therefore finally increases the electron density at the α-carbon.

For all monomers, the rate of insertion k_i is at least competitive with the rate of propagation k_p. This assumption is supported by the finding that signals for the first insertion product of the corresponding monomer with **11** or **12** dominate over all other higher insertion products.

Polymerizations. All polymerizations were carried out in toluene and proceeded in a living manner except for **4** and **5**. The polymerization of these two monomers start with a typical color change for an insertion from orange to deep purple. Within 5 min, the color reverts back to orange. GPC measurements revealed only the formation of short oligomers. This may result from either inter- or intramolecular metathesis reactions of the growing polymer with the internal (*Z*) or (*E*) double bond of the spacer. A description is given in Figure 5. Figures 6−8 show plots of molecular weight versus number of equivalents of the corresponding monomer. Excellent accordance with the calculated number average molecular weights (including end groups) were obtained. Polydispersities were within an acceptable range and comparable to those found for other β-insertion-based alkyne polymerizations.[16] Due to the fact that no polymerization system is absolutely perfectly living, Matyjaszewski[46] has suggested a ranking for living systems based on the ratios of the rate constants of chain transfer, propagation, and chain termination. Six different classes of polymerizations were presented. An arbitrarily chosen minimum lifetime, where ≤10% of the living polymer chains are deactivated, was defined as a limit for any well-defined system. According to our findings, the present polymerization systems are still active after 4 h. Thus, upon addition of a known amount of monomer, polymerizations are resumed. GPC measurements reveal no significant changes in the

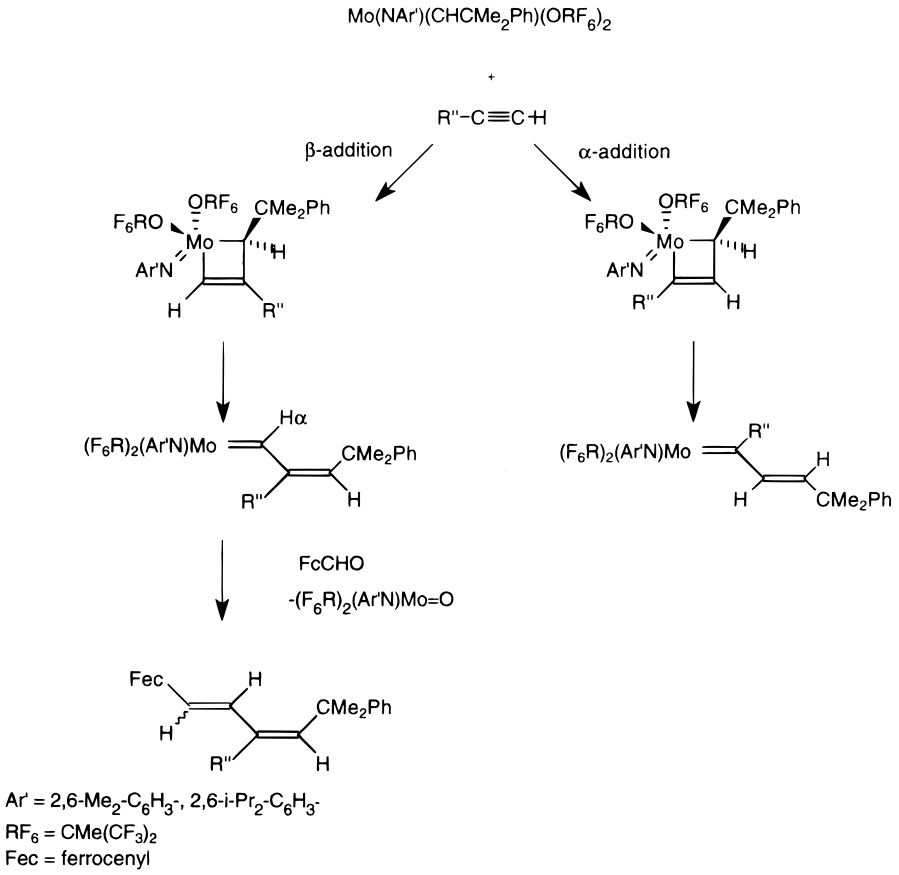


Figure 4. Insertion modes for terminal alkynes into a Schrock carbene.

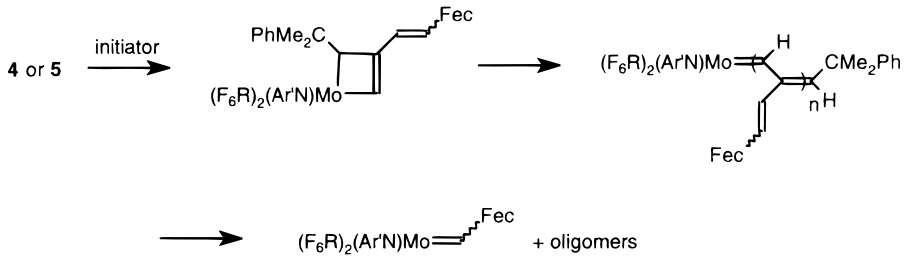


Figure 5. Termination of polymerization of compounds **4** and **5**.

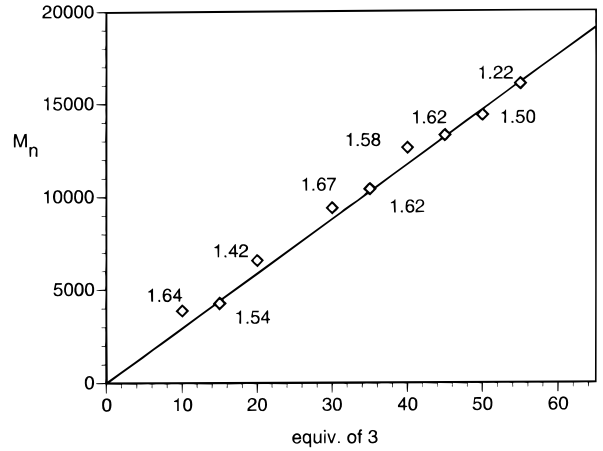


Figure 6. Plot of molecular weight (M_n) versus number of equivalents (N) of **3**. Data derived from Table 1. Experimental values (diamonds), calculated values (line).

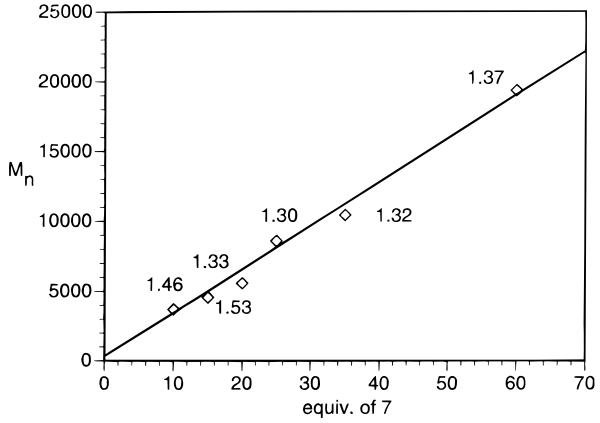


Figure 7. Plot of molecular weight (M_n) versus number of equivalents (N) of **7**. Data derived from Table 1. Experimental values (diamonds), calculated values (line).

polydispersities of the resulting polymers compared to those prepared in a one-step procedure. On the basis of these reaction times, the present systems satisfy at least a class 5 living system. Unfortunately, a correlation with the degree of polymerization (DP) is not possible, as the resulting polymers are only soluble up to DP $\approx$ 60.

For all reactions, chain termination ("capping") was performed by addition of ferrocene carboxaldehyde

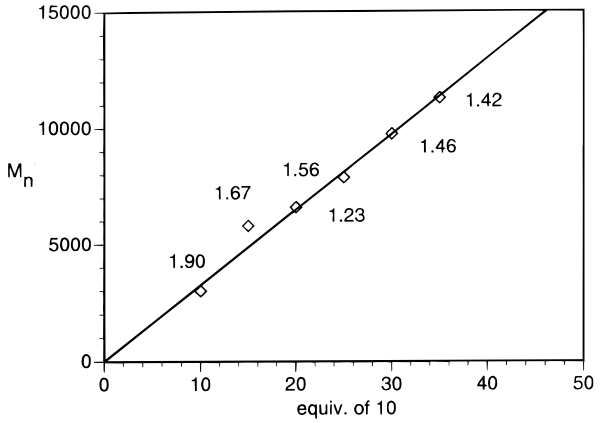


Figure 8. Plot of molecular weight (M_n) versus number of equivalents (N) of **10**. Data derived from Table 1. Experimental values (diamonds), calculated values (line).

(Figure 4). In the case of the capped first insertion products, (*E*)-configured double bonds are formed. On the basis of the above presented experimental evidence and previous findings,[16] we therefore conclude that polymerizations of less reactive, terminal acetylenes using molybdenum-based Schrock-type initiators may start either via α- or *β*-insertion and still be living. In contrast, the polymerization of highly active alkynes such as ethynylferrocene must start via α-addition in order to obtain favorable ratios of k_i/k_p.

Polymer Structure and Properties. The backbone of all polymers is apparently formed solely by head to tail connection of corresponding monomers, since no coupled signals for adjacent protons in the polymer backbone of the first or second insertion product have been observed. The absorption spectra of the final polymers are strongly dependent on the spacer. **3** forms highly colored, purple polymers with an absorption maximum (λ_{max}) around 515 nm. Molecular extinction coefficients (ϵ) are comparable to those of copolymers from ethynylferrocene and the Feast-monomer.[17] The finding that λ_{max} does not change significantly within 30 < DP < 55 suggests a maximum effective conjugation length (N_{eff}) ≤ 30. Π-stacking[27,50,51] of the adjacent phenyl rings as proposed for [2-(trimethylsilyl)phenyl]-acetylene[18,19] may serve as an explanation for the rather high value for N_{eff} compared to other metallocene-substituted poly-enes.[17] This effect is known to occur in solution with both mononuclear and oligonuclear systems. Calculations suggest typical inter-ring distances of approximately 3.1−3.5 Å for 1,3-diphenyl-substituted systems.[29] A description of the possible conformations of poly-**3** is shown in Figure 9. Stacked orientations as shown in Figure 9a seem highly unlikely, as the polymer possesses cis double bonds, which are known to rearrange into the thermodynamically more stable trans configuration. A stack as shown in Figure 9b having the substituent either at the same side or alternating on each side of the backbone would not be possible, as the ferrocenyl substituents are too close. A Π-arrangement as shown in Figure 9c would have an inter-ring distance for the phenyl substitutents of roughly 4 Å. If the *o*-ferrocenylphenyl substituent arranges in an alternating way with respect to the polymer backbone, this geometry would still provide sufficient space for the ferrocenyl groups, which show a distance between the two cyclopentadienyl rings of 3.32 Å. Nevertheless, other ways of Π-stacking involving the conjugated double bond cannot be ruled out.[30] Polymers of **3** can be prepared that contain up to approximately 60 equiv of monomer (Table 1). These poly-enes are soluble in any common solvent such as benzene, toluene, THF, or methylene chloride. They show a remarkable stability against air even in solution. Thus, solutions of (poly-**3**)$_{50}$ may be exposed to air for a few hours without any significant change in the UV spectrum.

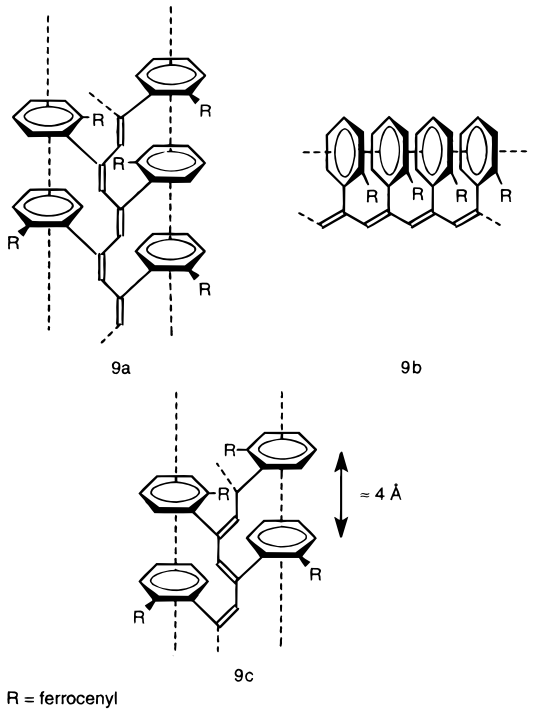


Figure 9. Possible Π-stacking arrangements for poly-**3**: 1,5-interactions (a, c) and 1,3 interactions (b).

Table 1. Polymerization Results for 3, 4, 5, 7, and 10[a]

	N	M_n(found)	M_n(calc)	PDI (M_w/M_n)	λ_{max} (nm) (ϵ) [L/(mol·cm)]
3[b]	10	3876	3190	1.64	
3[c]	15	4275	4620	1.54	499
3[b]	20	6580	6050	1.42	504
3[c]	30	9409	8910	1.67	515 (2.0×10^5)
3[c]	35	10422	10340	1.62	515 (2.1×10^5)
3[b]	40	12630	11770	1.58	511
3[b]	45	13301	13200	1.62	
3[b]	50	14386	14630	1.50	
3[c]	55	16062	16060	1.22	511
4[b]	5	1055	1510	1.28	480 (sh)
4[b]	15	3672	3870	1.35	315
5[b]	5	1349	1510	1.40	460 (sh)
5[b]	10	3000	2690	1.80	
7[b]	10	3714	3450	1.46	450 (sh)
7[c]	15	4575	5010	1.53	450 (sh)
7[b]	20	5598	6570	1.33	450 (sh)
7[c]	25	8609	8130	1.30	450 (sh) (7.7×10^4)
7[b]	35	10458	11250	1.32	450 (sh)
7[c]	60	19360	19059	1.37	453 (sh) (1.4×10^5)
10[b]	10	3014	3470	1.90	540
10[c]	15	5818	5040	1.67	534 (2.3×10^4)
10[b]	20	6610	6640	1.23	527
10[c]	25	7894	8180	1.56	533 (5.8×10^4)
10[c]	30	9782	9750	1.46	531 (4.4×10^4)
10[c]	35	11308	11356	1.42	531 (3.6×10^4)
10[b]	40	11041	12890	1.61	512

[a] All polymerizations were carried out in toluene using Mo(N−Ar′)(CMe$_2$Ph)(CMe(CF$_3$)$_2$)$_2$ as an initiator. [b] Ar′ = 2,6-Me$_2$-C$_6$H$_3$. [c] Ar′ = 2,6-i-Pr$_2$-C$_6$H$_3$. *N* = number of monomer equivalents added. sh (shoulder). [d] In THF.

The polymerization of **7** results in the formation of deep orange-red polymers with roughly the same properties in terms of solublity as poly-**3**. In contrast to poly-**3**, these polyenes show significantly reduced values for N_{eff} (<10). Apparently, the rather large, bulky side group prevents any significant conjugation.

Poly-**10** represents the first polymer containing ferrocenylazo groups. Compared to the poly-enes containing azobenzene side groups,[52] the solubility of poly-**10** is limited. The diazene group in each repetitive unit is believed to undergo both intramolecular and intermolecular interactions with other moieties. This not only aggravates the solubility of polymers with a DP > 40 in any common solvent but also impedes an effective conjugation in poly-**10**. As a direct consequence, even a decrease in λ_{max} with higher DP is observed. This is explained by the fact that **10** itself possesses a strong absorption maximum at $\lambda = 549$ nm that results from the highly conjugated, linear structure (Figure 3). The absorption maxima of poly-**10** result from an overlapping of the $\Pi-\Pi^*$ transition of the diazene group (549 nm) and the poly-ene backbone. Thus, at DP = 40, the (broad) absorption maximum has already dropped to $\lambda = 512$ nm. Based on the findings for poly-**7**, the actual maximum for the $\Pi-\Pi^*$ transition of the double bonds in the backbone of this poly-ene is estimated to be within 440 and 470 nm.

The present investigation underlines the broad applicability of molybdenum-based Schrock carbenes for the polymerization of terminal acetylenes. Deactivation of the alkyne unit by separating the ferrocene moiety with a spacer allows the generation of a living polymerization system despite the β-addition of the monomer to the initiator. Unfortunately, longer spacers also lead to enhanced steric 1,3-interaction. Specifically phenylvinyl, azoarylene, and ethenediyl spacers did not enhance N_{eff}. Nevertheless, an ortho-substituted phenyl spacer positively influences conjugation, possibly via Π-stacking. Similar studies including methylated ferrocenylalkynes as reversible electrophores and thiophenes as superior NLO spacers or OLED constituents will be reported in due course.

Experimental Section

General Details. All experiments were performed under an argon atmosphere by standard Schlenk techniques unless stated otherwise. Reaction solvents were purified by standard methods. Purchased starting materials were used without any further purification. Pentane was washed with sulfuric/nitric acid (95/5 v/v), sodium bicarbonate, and then water, stored over calcium chloride, and then distilled from sodium benzophenone ketyl under nitrogen. Reagent grade diethyl ether, tetrahydrofuran, toluene, and benzene were distilled from sodium benzophenone ketyl under nitrogen. Reagent grade dichloromethane was distilled from calcium hydride under argon. All deuterated NMR solvents were dried by appropriate methods prior to use. Mo(*N*-2,6-*i*-$Pr_2C_6H_3$)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$ (**11**) and Mo(*N*-2,6-$Me_2C_6H_3$)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$ (**12**) were synthesized as described in the literature.[53]

NMR data were obtained in the indicated solvent at 30 °C on a Bruker AM 300 unless stated otherwise and are listed in parts per million downfield from tetramethylsilane for proton and carbon. Coupling constants are given in Hertz. IR spectra were recorded on a Midac FT-IR. Mass spectra were obtained on a Finnigan MAT 95 and a CH-7 (MAT). GPC data were determined in THF using a 484 UV−vis detector, a 717 autosampler, a column heater (35 °C), a 510 HPLC pump, a 490E UV detector, a 410 RI detector, and a Millenium work package (all Waters).

X-ray Measurement and Structure Determination of 3, 6, 7, and 8. A Siemens P4 diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 71.073$ pm) was used for data collection. Intensities were measured via ω-scans and corrected for Lorentz and polarization effects. The structures were solved by direct methods (SHELXS-86)[54] and refined by full matrix least-squares against F^2 (SHELXL-93).[55] The function minimized was $\Sigma[w(F_o^2 - F_c^2)^2]$ with the weight defined as $w^{-1} = [\sigma^2(F_o^2) + (xP)^2 + yP]$ and $P = (F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined with anisotropic displacement parameters except for the carbon atoms of the C_5H_5 groups in **3**, which were refined isotropcally. All hydrogen atoms were located by difference Fourier methods; however, in the refinement they were generated geometrically and refined with isotropic displacement parameters 1.2 times higher than *U*(eq) of the attached C atoms. The carbon atoms of the double bond in **3** are disordered in a ratio 1:1 for C(11a) and C(11b) and also C(12a) and C(12b). Further crystallographic data are collected in Table 2.

Methyl 2-Ferrocenylbenzoate[56] [1294−22−0]: 2-Ferrocenylbenzoic acid was prepared as described in the literature.[57] 2-Ferrocenylbenzoic acid (10 g, 33 mmol) was dissolved in 50 mL of methanol. Sulfuric acid (1 mL) was added, and the mixture was refluxed overnight. A saturated solution of sodium bicarbonate (100 mL) was added, and the mixture was extracted with diethyl ether. After drying over Na_2SO_4, the ether was evaporated in vacuo to yield 10 g (95%) of the ester. Mp: 124−125 °C. Spectroscopical data were identical with those reported in the literature.

2-Ferrocenylbenzyl Alcohol (1). Methyl 2-ferrocenylbenzoate (19 g, 31.2 mmol) was dissolved in 100 mL of THF, and $LiAlH_4$ (0.4 g, 10.5 mmol) was added. The solution was stirred overnight. Water (5 mL) was added, and the mixture was extracted with diethyl ether. Evaporation of the diethyl ether yielded 5.1 g (56%) of **1**. Attempts to crystallize **1** have failed so far. Nevertheless, the oily product was clean enough for further syntheses. IR (KBr): 3094 (w), 1634 (s), 1385 (s), 1107 (s), 1032 (s), 1005 (s), 820 (s), 764 (s), 490 (s). ^{1}H NMR ($CDCl_3$): δ 3.0 (bs, O*H*), 4.05 (s, 5 H Cp), 4.20 (t, 2 H, $J = 1.8$), 4.44 (t, 2 H, $J = 1.8$), 4.60 (s, 2 H), 7.16−7.28 (m, 4 H, Ar). ^{13}C NMR ($CDCl_3$): δ 64.2, 68.8, 69.0, 70.2, 70.5, 127.2, 128.7, 129.3, 129.7, 131.2, 131.6. MS (EI, 70 eV): calcd for $C_{17}H_{16}FeO$ 292.055; found $m/z = 292$ ($M^{\bullet+}$, 100%).

2-Ferrocenylbenzaldehyde (2). 2-Ferrocenylbenzyl alcohol (5.1 g, 17.5 mmol) was dissolved in 50 mL of dichloromethane, and freshly precipitated MnO_2 (10 g) was added. After stirring for 24 h, a quantitative conversion of the alcohol into the aldehyde was observed by TLC. Removal of the solvent and flash chromatography over silica G-60 (200−400 mesh) yielded 2.8 g (55.3%) of **2**. Mp: 59−60 °C. IR (KBr): 1684 (s), 1589 (m), 1495 (m), 1259 (vs), 1194 (m), 1105 (vs), 1010 (s), 803 (vs), 689 (m). ^{1}H NMR ($CDCl_3$): δ 3.50 (s, 5 H Cp), 3.76 (t, 2 H, $J = 1.8$), 3.89 (t, 2 H, $J = 1.8$), 6.6−7.3 (m, Ar), 9.80 (s, 1 H, C*H*O). ^{13}C NMR ($CDCl_3$): δ 69.6, 71.3, 83.7, 70.3, 126.7, 127.6, 132.0, 133.3, 134.4, 143.4, 192.7. UV (CH_3CN) (λ_{max} [nm], ϵ): 227 (25 449), 248 (15 540), 276 (81 150), 295 (6619), 379 (1302). MS (EI, 70 eV): calcd for $C_{17}H_{14}FeO$ 290.039; found $m/z = 290$ ($M^{\bullet+}$, 100%).

Note: Even with diisobutylaluminum hydride complete reduction to the alcohol is favored. Therefore, a two-step protocol involving a reoxidation of the alcohol to the corresponding aldehyde is advantageous.

(2-Ethynylphenyl)ferrocene (3). The compound was prepared in analogy to a published one-pot procedure.[36] Potassium *tert*-butoxide (1.0 g, 11.1 mmol) was added to a solution of (chloromethyl)triphenylphosphonium iodide (2.27 g, 4.2 mmol) in 30 mL of THF at room temperature. After 15 min a deep yellow color developed.[34,35] 2-Ferrocenylbenzaldehyde (1.2 g, 4.1 mmol) was added, and the solution was refluxed for 14 h. Evaporation of the solvent, dissolution in pentane:diethyl ether (80:20) and flash chromatography over silica G 60 yielded 0.8 g (68%) of **3**. FT-IR (KBr): 3278 (s), 3065 (m), 2100 (s), 1594 (m), 1498 (s), 1456 (m), 1429 (n), 1105 (s), 1002 (s), 819 (vs), 760 (vs), 620 (bs). ^{1}H NMR (C_6D_6): δ 3.30 (s, 1 H, CC*H*), 4.10 (s, 5 H, Cp), 4.32 (t, 2 H, $J = 1.8$),

Table 2. Crystal Data and Structure Refinement for Compounds 3, 7, and 8

	3	7	8
mol formula	$C_{18}H_{14}Fe$	$C_{20}H_{16}Fe$	$C_{16}H_{13}BrFeN_2$
fw	286.14	312.18	369.04
cryst syst	orthorhombic	monoclinic	monoclinic
space group	$P2_12_12_1$ (No. 19)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
unit cell dimens			
a, pm	880.2(3)	599.9(4)	1245.2(2)
b, pm	1008.2(3)	1991.9(6)	1063.3(2)
c, pm	3015.7(15)	1263.7(4)	1147.9(1)
β, deg		100.76(5)	114.21(1)
vol, nm^3	2.676(2)	1.4835(12)	1.3862(4)
Z	8	4	4
temp, K	213	218	213
density (calcd), Mg/m^3	1.420	1.398	1.768
abs coeff, mm^{-1}	1.108	1.006	3.959
F(000)	1184	648	736
color, habit	orange prism	red needle	black prism
cryst size, mm	0.4 × 0.25 × 0.15	0.82 × 0.17 × 0.08	0.5 × 0.25 × 0.16
θ range for data collcn, deg	2.68−20.5	2.62−21.0	3.56−25.0
index range	$-1 \le h \le 8$, $-1 \le k \le 10$, $-29 \le l \le 24$	$0 \le h \le 5$, $-1 \le k \le 20$, $-12 \le l \le 12$	$-12 \le h \le 13$, $-11 \le k \le 0$, $-12 \le l \le 0$
no. of rflns collcd	3229	1861	2230
no. of indep rflns	2490	1547	2126
no. of rflns with $I > 2\sigma(I)$	2041	1243	1770
abs corr	none	ψ scan	ψ scan
max., min transm		0.948, 0.867	0.975, 0.741
refinement method	full-matrix least squares on F^2		
params	293	213	182
goodness of fit on F^2	1.061	1.101	1.028
final *R* indices ($I > 2\sigma(I)$)	$R1 = 0.0436$	$R1 = 0.0417$	$R1 = 0.0282$
	$wR^2 = 0.0792$	$wR^2 = 0.0984$	$wR^2 = 0.0577$
largest diff peak and hole, e nm^{-3}	426, −228	399, −224	392, −348

4.94 (t, 2 H, $J = 2.2$), 7.10−7.33 (m, 2 H), 7.47 (d, 1 H, $J = 7.6$), 7.59 (d, 1 H, $J = 7.8$). ^{13}C NMR (C_6D_6): δ 68.64, 69.0, 69.7, 80.0, 81.1, 84.4, 125.6, 128.4, 129.0, 134.6. HRMS: calcd for $C_{18}H_{14}Fe$ 286.0445; found 286.0438 ($M^{\bullet+}$, 100%), 221.002 ($M^{\bullet+} - C_5H_5$, 15.4%), 165.070 ($M^{\bullet+} - FeC_5H_5$, 28.1%). UV (CH_2Cl_2) (λ_{max} [nm], ϵ): 294.5 (12 400), 352.5 (1380), 452.5 (200). Anal. calcd. for $C_{18}H_{14}Fe$ ($M_w = 286.156$): C, 75.55; H, 4.93. Found: C, 75.34; H, 5.08.

(*Z*,*E*)-But-1-en-3-ynylferrocene (4, 5). The compound was prepared analogously to a published one-pot procedure.[36] Potassium *tert*-butylate (2.308 g, 20.6 mmol) was added to a solution of (ferrocenylmethyl)triphenylphosphonium iodide[58] (11.00 g, 18.7 mmol) in THF (50 mL) at −70 °C. The mixture was warm at room temperature to 0 °C and then stirred for 30 min. Propargyl carbaldehyde[59,60] (1.08 mL, 1.061 g, $d = 0.986$, 19.6 mmol, 1.05 mol equiv) was added via a syringe, and the deep red suspension was warmed to room temperature and stirred for 1 h. The solvent was removed in vacuo, and the residue was extracted with saturated NH_4Cl solution and CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The crude red product was purified by column chromatography using neutral alumina (5% H_2O, 3 × 30 cm) as the stationary phase and *n*-hexane as the mobile phase to separate it from all byproducts. *n*-hexane:diethyl ether = 50:50 was used for the separation of the two isomers to yield (*Z*)-but-1-en-3-ynylferrocene (0.747 g, 17%) and (*E*)-but-1-en-3-ynylferrocene (0.707 g, 16%) as red solids. The (*Z*)-isomer was eluted first. The (*E*)/(*Z*) ratio of the two isomers was approximately 5:4.

(*Z*)-But-1-en-3-ynylferrocene (4). Mp: 72−73 °C. IR (KBr): 3272 (s), 3083 (w), 2080 (w), 1602 (m), 1106 (m), 1040 (m), 1028 (m), 1001 (m), 820 (vs), 778 (m), 670 (m), 621 (m), 504 (m), 479 (s). ^1H NMR ($CDCl_3$): δ 3.34 (s, 1 H, C≡C*H*), 4.15 (s, 5 H, Cp), 4.30 (t, 2 H), 4.82 (t, 2 H), 5.45 (d, $J = 12$ Hz, 1 H), 6.51 (d, $J = 12$ Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ 69.2, 69.3 (Cp), 69.4, 80.0, 82.8 (C≡*C*H), 82.9, 102.6, 140.4. HRMS (EI): calcd for $C_{14}H_{12}Fe$ 236.029; found $m/z = 236.029$ ($M^{\bullet+}$, 100%). UV (CH_2Cl_2) (λ_{max} [nm], ϵ): 248.5 (11 700), 294.5 (11 400), 355 (933), 457 (530).]

(*E*)-But-1-en-3-ynylferrocene (5). Mp: 80−81 °C. IR (KBr): 3298 (s), 2962 (m), 2931 (m), 2095 (w), 1727 (vs), 1615 (s), 1285 (vs), 1279 (vs), 1125 (m), 949 (m), 741 (m), 643 (m), 513 (s). ^1H NMR ($CDCl_3$): δ 2.98 (s, 1 H, C≡C*H*), 4.13 (s, 5 H, Cp), 4.27 (t, 2 H), 4.35 (t, 2 H), 5.70 (d, $J = 16$ Hz, 1 H), 6.82 (d, $J = 16$ Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ 67.0, 69.3, 69.7 (Cp), 77.4 (C≡*C*H), 81.1, 83.6, 103.5, 142.5. MS (70 eV): calcd for $C_{14}H_{12}Fe$ 236.029; found m/z 236 ($M^{\bullet+}$, 100%). UV (CH_2Cl_2) (λ_{max} [nm], ϵ): 247 (9550), 299.5 (9772), 340 (1862), 458.5 (794). Anal. Calcd for $C_{14}H_{12}Fe$: C, 71.22; H, 5.12. Found: C, 71.41; H, 5.36.

4-[2-(Ferrocenyl)vinyl]benzaldehyde [123931-08-8]. In contrast to the procedure described in the literature,[32,33,61] a modified synthesis was performed. Potassium *tert*-butylate (0.135 g, 1.20 mmol) was added to a suspension of (ferrocenylmethyl)triphenyl phosphonium tetrafluoroborate[58−61] (0.600 g, 1.09 mmol) in dry THF (30 mL) at −70 °C. The mixture was allowed to warm to 0 °C and was stirred for 30 min. Benzene-1,4-dicarboxaldehyde (0.587 g, 4.38 mmol) was added, and the red suspension was warmed to room temperature and stirred for 1 h. The solvent was removed in vacuo, and the residue was extracted with saturated NH_4Cl solution and CH_2Cl_2. The organic layer was dried over Na_2SO_4, and the crude red product was purified by column chromatography using basic alumina, (5% H_2O, 3 × 25 cm) as the stationary phase and *n*-hexane/CH_2Cl_2 = 1:1 as the mobile phase to separate the (*E*)/(*Z*) mixture from other byproducts. *p*-Toluenesulfonic acid (0.045 g, 0.237 mmol, 0.2 mol equiv) was added to a solution of the (*E*)/(*Z*) isomers in O_2-free toluene (100 mL). After the mixture was refluxed for 1 h, the organic layer was quenched with saturated $NaHCO_3$ solution. Washing with water, drying with Na_2SO_4 and removal of the solvent in vacuo yielded the aldehyde as a red solid (0.240 g, 69%). Mp: 159−161 °C. Spectroscopic data were identical with those reported in the literature.

(*E*,*Z*)-1-Chloro-2-[4-(2-ferrocenylvinyl)phenyl]ethene (6). Potassium *tert*-butylate (0.125 g, 1.11 mmol, 1.1 mol equiv) was added to a suspension of (chloromethyl)triphenylphosphonium chloride (0.351 g, 1.01 mmol) in dry THF (20 mL) at −70 °C. The mixture was allowed to warm to 0 °C and stirred for 30 min. 4-(2-Ferrocenylvinyl)benzaldehyde (0.160 g, 0.51 mmol) was added, and the red suspension was warmed to room temperature and stirred for 1 h. The solvent was removed in vacuo, and the residue was extracted with saturated NH_4Cl solution and ether. The organic layer was

dried over Na_2SO_4, and the crude red product was purified by column chromatography using basic alumina (5% H_2O, 4.5 × 8 cm) as the stationary phase and *n*-hexane as the eluent. The (*E*)/(*Z*) ratio of the two isomers was approximately 1:1. Removal of the solvent in vacuo yielded **6** as an orange solid (0.126 g, 71%). IR (KBr): 3064 (w), 3031 (w), 1630 (m), 1600 (m), 1349 (m), 1106 (m), 955 (s), 826 (vs), 814 (vs), 789 (s), 484 (m). ^{1}H NMR ($CDCl_3$): δ 4.13 (s, 10 H, Cp), 4.28 (t, 4 H), 4.46 (t, 4 H), 6.23 (d, J = 8 Hz, 1 H), 6.60 (d, J = 8 Hz, 1 H), 6.63, 6.68, 6.73, 6.88, 6.91 (each d, J = 16 Hz and J = 6 Hz, 7 H), 7.24 (d, 2 H, Ar), 7.40 (dd, J = 9 Hz, 4 H, Ar), 7.65 (d, 2 H, Ar). ^{13}C NMR ($CDCl_3$): δ 66.9, 69.2, 69.2 (Cp), 83.1, 117.0, 118.0, 125.3, 125.4, 125.6, 126.1, 126.4, 127.6, 127.8, 129.0, 129.6, 132.2, 133.0, 137.8. HRMS (EI): calcd for $C_{20}H_{17}ClFe$ 348.037; found m/z 348.037 ($M^{\bullet+}$, 100%).

2-(4-Ethynylphen-1-yl)vin-1-ylferrocene (7). Potassium *tert*-butylate (0.064 g, 0.57 mmol, 2 mol equiv) was added to a solution of (*E*,*Z*)-1-chloro-2-[4-(2-ferrocenylvinyl)phenyl]ethene (0.100 g, 0.28 mmol, 1 mol equiv) in dry THF (40 mL).[36] The mixture was refluxed overnight. The solvent was removed in vacuo, and the residue was extracted with saturated NH_4Cl solution and ether. The organic layer was washed with saturated NaCl solution and dried with Na_2SO_4. Removing the solvent yielded **7** as a red solid (0.089 g, 99%). Mp: 149−150 °C. IR (KBr): 3265 (w), 2964 (w), 2923 (w), 2101 (w), 1632 (m), 1600 (m), 1106 (m), 1044 (m), 1027 (m), 826 (s), 821 (vs), 791 (m), 484 (m). ^{1}H NMR ($CDCl_3$): δ 3.11 (s, 1 H, C≡C*H*), 4.13 (s, 5 H, Cp), 4.29 (t, 2 H), 4.45 (t, 2 H), 6.65 (d, J = 16 Hz, 1 H), 6.90 (d, J = 16 Hz, 1 H), 7.35 (d, 2 H, Ar), 7.43 (d, 2 H, Ar). ^{13}C NMR ($CDCl_3$): δ 67.0, 69.2 (Cp), 69.3, 77.5, 82.8 (C≡*C*H); 84.0, 120.0, 125.1, 125.5, 128.5, 132.4, 138.4. HRMS (EI): calcd for $C_{20}H_{16}Fe$ 312.060; found m/z 312.061 ($M^{\bullet+}$, 51.3%). UV (CH_2Cl_2) (λ_{max} [nm], ϵ): 228 (11 220), 276 (7944), 324 (16 596), 462.5 (1259). Anal. Calcd for $C_{20}H_{16}Fe$ (M_w = 312.194): C, 76.95; H, 5.17; N, 0.00. Found: C, 76.56; H, 5.50; N, 0.00.

1-(4-Bromophenyl)-2-ferrocenyldiazene (8). Purified ferrocenyllithium[62] (0.705 g, 3.76 mmol) was added to a solution of 4-bromobenzendiazonium tetrafluoroborate (1.194 g, 4.41 mmol) in dry THF (100 mL) at −78 °C. The stirred solution was allowed to warm to room temperature. After the solution was stirred for 2 h at room temperature, the solvent was removed in vacuo. The reaction mixture was extracted with Et_2O/H_2O and dried over Na_2SO_4. After filtration and removal of the solvent by rotary evaporation, the dark violet solid was purified by column chromatography using neutral alumina (5% H_2O, 4 × 25 cm) as the stationary phase and *n*-hexanes as the eluent to yield **8** as a dark violet solid (0.460 g 34%). Mp: 168−172 °C. IR (KBr): 3106 (w), 2963 (w), 1582 (m), 1570 (m), 1478 (m), 1418 (s), 1391 (m), 1369 (s), 1246 (m), 1215 (m), 1109 (m), 1099 (m), 1067 (s), 1026 (s), 1007 (vs), 939 (s), 833 (vs), 821 (vs), 808 (vs), 758 (s), 710 (s), 644 (s). ^{1}H NMR ($CDCl_3$): δ 4.22 (s, 5 H, Cp), 4.49 (t, 2 H), 5.04 (t, 2 H), 7.56 (d, J = 8 Hz, 2 H, Ar), 7.74 (d, J = 8 Hz, 2 H, Ar). ^{13}C NMR ($CDCl_3$): δ 65.3, 70.0 (Cp), 70.6, 123.1, 132.3. HRMS (EI): calcd for $C_{16}H_{13}BrFeN_2$ 367.961; found m/z 369.973 (100% $M^{\bullet+}$), 289.927 ($M^{\bullet+}$ − Br, 56.0%), 185.004 ($Fc^{\bullet+}$).

1-Ferrocenyl-2-(4-(2-(trimethylsilyl)ethynyl)phenyl)-diazene (9). (Trimethylsilyl)acetylene (0.05 mL, 0.38 mmol, 1.4 mol equiv, d = 0.695), triethylamine (1 mL, d = 0.726), and bis(triphenylphosphine)palladium(II) chloride (0.005 g)[63] were added to a solution of 1-(4-bromophenyl)-2-ferrocenyl-diazene (0.100 g, 0.27 mmol, 1 mol equiv) in dry DMF (30 mL). The solution was heated to 90 °C for 4 h. The solvent was removed in vacuo, and the reaction mixture was extracted with Et_2O/H_2O and dried over Na_2SO_4. After filtration and removal of the solvent by rotary evaporation, the solid was purified by column chromatography using neutral alumina (5% H_2O, 4 × 2 cm) as the stationary phase and *n*-hexanes as the eluent to yield **9** as a violet solid (0.100 g 96%). Mp: 106−108 °C. IR (KBr): 2153 (*C*−*C*). ^{1}H NMR ($CDCl_3$): δ 0.20 (m, 9 H), 4.21 (s, 5 H, Cp), 4.57 (t, 2 H), 5.05 (t, 2 H), 7.50 (d, 2 H, Ar), 7.66 (d, 2 H, Ar). ^{13}C NMR ($CDCl_3$): δ 1.01 (Si(*C*H_3)$_3$), 65.3, 70.0 (Cp), 70.6, 87.6, 89.6, 121.7, 130.6, 132.9, 159.4 (Ar). HRMS (EI): calcd for $C_{21}H_{22}FeN_2Si$ 386.090; found m/z 386.091 ($M^{\bullet+}$, 82.8%), 209.078 (100%).

1-Ferrocenyl-2-(4-ethynylphenyl)diazene (10). Tetrabutylammonium fluoride (0.66 mL, 0.72 mmol, 1.2 mol equiv) was added to a solution of 1-ferrocenyl-2-(4-(2-(trimethylsilyl)ethynyl)phenyl)diazene (232 mg, 0.60 mmol, 1 mol equiv) in dry THF (150 mL). The solution was refluxed for 15 h. The solvent was removed in vacuo, and the reaction mixture was extracted with Et_2O/H_2O and dried over Na_2SO_4. After filtration and removal of the solvent by rotary evaporation, the solid was purified by column chromatography using neutral alumina (5% H_2O, 4 × 2 cm) as the stationary phase and *n*-hexanes as the mobile phase. Recrystallization from *n*-hexanes yielded 0.91 g (48%) of **10** as a violet solid. Mp: 114−116 °C.

Note: The trimethylsilylated ethyne shows remarkable inertness toward deprotection. For instance, reaction with CsF in refluxing dioxane gave no satisfactory conversion to **10**.

IR (KBr): 3276 (*C*−*H*), 2099 (*C*−*C*). ^{1}H NMR ($CDCl_3$): δ 3.20 (s, 1 H, alkyne), 4.23 (s, 5 H, Cp), 4.60 (t, 2 H), 5.07 (t, 2 H), 7.56 (d, 2 H, Ar), 7.72 (d, 2 H, Ar). ^{13}C NMR ($CDCl_3$): δ 65.3, 70.0, 70.7 (Cp), 78.7, 121.6, 133.0. HRMS (EI): calcd for $C_{18}H_{14}FeN_2$ 314.051; found m/z 314.050 ($M^{\bullet+}$, 100%). UV (CH_2Cl_2) (λ_{max} [nm], ϵ): 333.5 (18872.82), 549 (2934.41). Anal. Calcd for $C_{18}H_{14}FeN_2$: C, 68.82; H, 4.49; N, 8.92. Found: C, 68.87; H, 4.18; N, 8.83.

Polymerizations. The following procedure is typical: The monomer (30 mg) was dissolved in toluene (10 mL), and a solution of the corresponding amount of the initiator in toluene (0.5−5 mL) was added to the well-stirred solution. The color of the reaction mixture changed from yellow-orange to deep red within a few minutes. It was stirred for 6 h, ferrocenecarboxaldehyde was added, and stirring was continued for an additional 30 min. Finally, the reaction mixture was poured into pentane and the precipitate was washed with diethyl ether to remove unreacted ferrocenecarboxaldehyde and then was dried in vacuo. Except for **4** and **5**, yields were ≥95%.

Investigation of the Type of Insertion. The initiator (10 mg) was added to a solution of the monomer (1.5 equiv) in C_6D_6 (0.7 mL). The reaction mixture turned deep red immediately and was ready for NMR experiments. In the case of β-addition, ferrocene carboxaldehyde (50 mg, 0.24 mmol) was added to the first insertion product after 1 h.

3 reacts with Mo(*N*-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(OC$Me(CF_3)_2)_2$ via α-addition. No new alkylidene resonances are observed. ^{1}H NMR (C_6D_6) δ 6.19 (d, J = 16), 6.04 (d, J = 16). **3** reacts with Mo(*N*-2,6-*i*-$Pr_2C_6H_3$)(CHCMe_2Ph)(OC$Me(CF_3)_2)_2$ via β-addition. New alkylidene resonances at δ 12.48 (s, Mo=C*H*R) and 10.51 (s, Mo=C*H*R) as well as signals for the γ-protons at 6.22 (s), 6.17 (s), and 5.73 (s) are observed. Poly-**3**: ^{1}H NMR (C_6D_6) δ 8.0−6.0 (m), 5.0−3.5 (m).

4 reacts with Mo(*N*-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(OC$Me(CF_3)_2)_2$ via β-addition. ^{1}H NMR (C_6D_6): δ 12.64 (s, Mo=C*H*R), 12.26 (s, Mo=C*H*R).

7 reacts with Mo(*N*-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(OC$Me(CF_3)_2)_2$ via β-addition. ^{1}H NMR (C_6D_6): δ 14.04 (s, Mo=C*H*R), 12.72 (s, Mo=C*H*R), 12.36 (s, Mo=C*H*R), 12.15 (s, Mo=C*H*R), 5.72 (s). Capping with ferrocenecarboxaldehyde yields a product with a trans double bond: δ 6.17 (d, J = 16.2), 6.07 (d, J = 16.2), 5.72 (s). **7** reacts with Mo(*N*-2,6-*i*-$Pr_2C_6H_3$)(CHCMe_2Ph)(OC$Me(CF_3)_2)_2$ via β-addition. ^{1}H NMR (C_6D_6): δ 15.07 (s, Mo=C*H*R), 10.93 (s, Mo=C*H*R), 5.73 (s). Capping with ferrocenecarboxaldehyde yields a product with a trans double bond: δ 6.17 (d, J = 16.2), 6.07 (d, J = 16.2), 5.72 (s). Poly-**7**: ^{1}H NMR (C_6D_6) δ 7.8−7.6 (bm) (Ar), 4.3 (bm), 4.0 (bs) (Cp).

10 reacts with Mo(*N*-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(OC$Me(CF_3)_2)_2$ via β-addition. ^{1}H NMR (C_6D_6): δ 13.72 (s, Mo=C*H*R), 12.75 (s, Mo=C*H*R), 12.28 (s, Mo=C*H*R), 5.73 (s). The ferrocene carboxaldehyde-capped product shows signals at δ 6.15 (d, J = 12.5), 5.75 (d, J = 12.5), and 5.73 (s). **10** reacts with Mo(*N*-2,6-*i*-$Pr_2C_6H_3$)(CHCMe_2Ph)(OC$Me(CF_3)_2)_2$ via β-addition. ^{1}H NMR (C_6D_6): δ 15.03 (s, Mo=C*H*R), 14.41 (s, Mo=C*H*R), 12.93 (s, Mo=C*H*R), 12.68 (s, Mo=C*H*R), 12.49 (s, Mo=C*H*R), 11.72 (s, Mo=C*H*R), 11.60 (s, Mo=C*H*R), 5.73 (s). The fer-

rocene carboxaldehyde-capped product shows signals at δ 6.20 (d, J = 16.2), 6.11 (d, J = 16.2), 5.73 (s). Poly-**10**: ^{1}H NMR (C_6D_6) δ 8.3−7.0 (m), 5.2 (bm), 4.4−4.0 (m).

Supporting Information Available: Supporting Information Available: Complete crystallographic data of **3**, **6** [123931-08-8], **7**, and **8** are deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, Lensfield Road, Cambridge CB2 1EW, U.K.

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