Use of the Extended One-Pot (EOP) Procedure for the Preparation of Ethynylated Thiophene Derivatives and Related Palladium−Ethynylthiophene Organometallic Oligomers

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The palladium-catalyzed coupling (Stille coupling) of 2,5-diiodothiophene (**1**) with tributyl(ethynyl)tin forms the 2,5-bis(ethynyl)thiophene (**3**) and tributyltin iodide as side product (step 1). Addition of lithium diisopropylamide (LDA) to this mixture causes deprotonation of the bis-alkyne and its reaction with the tin halide present in the medium to form the 2,5-bis[(tributyltin)ethynyl]thiophene (**4**) (step 2). To this mixture was subsequently added *trans*-dichlorobis(tri-*n*-butylphosphine)palladium (**5**), and the corresponding *trans*-bis(tri-*n*-butylphosphine)-μ-[2,5-bis(ethynyl)thiophene]palladium oligomer (**6**) was obtained (step 3). Alternatively, the same route can be directed toward the formation of ethynylated thiophene oligomers: after formation of the 2,5-bis[(tributyltin)ethynyl]thiophene (**4**) (step 2), addition of 2-iodothiophene (**8**) or 2-iodo-5-(trimethylsilyl)thiophene (**10**) led to the formation of 2,5-bis(2-thienylethynyl)thiophene (**9**) (step 3) and [2-trimethylsilyl(ethynyl)-thiophene]-2,5-bisethynylthiophene (**11**) (step 3′), respectively. The latter can be easily desilylated to obtain the [2-(ethynyl)thiophene]-2,5-bisethynylthiophene (**13**), while treatment of **9** with *sec*-BuLi/I_2 formed the 2,5-[2,2′-(5,5′-diiodo)bisthienyl]bisethynylthiophene (**12**). Through a sequence of transformations similar to steps 1−3, the oligo(iodo)ethynylthiophene **12** has been connected to the bis(tri-*n*-butylphosphine)palladium moiety to form the *trans*-bis(tri-*n*-butylphosphine)-μ-[2,2′-bis(ethynyl)thiophene]-2,5-bisethynylthiophene]palladium polymer (**15**). To compare the advantages of the above extended one-pot (EOP) procedures over classical routes, polymers **6** and **15** were also prepared by the copper-catalyzed reaction of *trans*-dichlorobis(tri-*n*-butylphosphine)palladium (**5**) with 2,5-bis(ethynyl)thiophene (**3**) and [2-(ethynyl)thiophene]-2,5-bisethynylthiophene (**13**).

Introduction

Organometallic polymers having a backbone composed of conjugated polyynes and transition metals are attracting increasing attention in material science because they may exhibit liquid crystalline,[1] magnetic,[2] optical,[3] and electronic properties.[4] These technologically important characteristics arise from the unique electronic delocalization in these materials along the entire polymer backbone, including metal atoms and bridging acetylide spacers. Because of these important potential applications, efficient routes to organometallic conjugated polymers are required.

Preparation of polymeric materials of type $[-C{\equiv}C-M-C{\equiv}C-Ar-]_n$ (M = Ni, Pd, Pt) was first developed by Hagihara[5] by means of a dehydrohalogenation reaction using Cu-catalyzed coupling of terminal alkynes ($H-C{\equiv}C-Ar-C{\equiv}C-H$) and transition metal halides (L_2MCl_2). Although this procedure is quite efficient and has also allowed the preparation of polymers containing mixed metals into the polymer backbone,[5c] this synthetic route suffers from a major drawback of preparing and handling pure terminal alkynes, which are quite reactive materials, occasionally manifesting uncontrollable reactivity.[6] Terminal alkynes are also used for the preparation of polymers containing Pt−Pt bonds, and gold-containing polymers obtained by Puddephatt;[7] the

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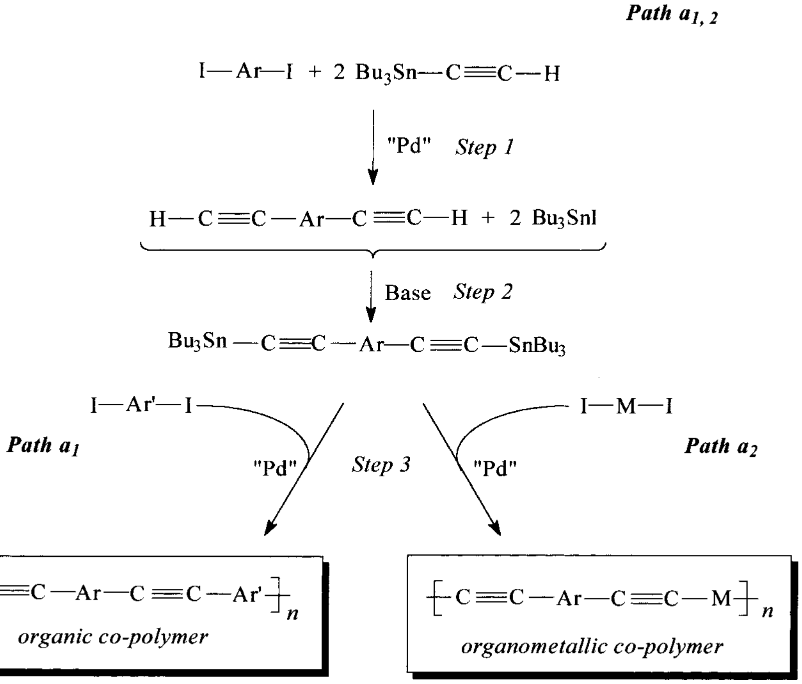
Scheme 1



latter are prepared from the reaction of metal chlorides with the appropriate diethynylarene (H−C≡C−Ar−C≡C−H) in the presence of a base. Also Marder and coworkers[8] have made use of terminal dialkynes to form rhodium-containing polyynes which are obtained by reductive elimination of methane and loss of a phosphine ligand in the reaction of unsubstituted diynes (H−C≡C−Ar−C≡C−H) and $Rh(PR_3)_4Me$.

Recently Lewis[9] has proposed an alternative route to linear-chain, metal-containing polymers based on the polycondensation of bis(trimethylstannyl)diynes ($Me_3Sn{-}C{\equiv}C{-}Ar{-}C{\equiv}C{-}SnMe_3$) with metal halides.

With respect to Hagihara's procedure, Lewis' method was extended to Fe, Ru, Os, Rh, and Co, in addition to group 10 metals. However if the Lewis synthetic approach widened the array of organometallic polymers attainable, it also introduced the demanding necessity of transformation of the alkynes into the corresponding trimethyltin derivatives. Such a transformation must be unavoidably performed by using noxious tin reagents. Moreover, after the formation of the polymeric products, one must deal with the trimethyltin chloride side product, the most toxic tin reagent.[10]

More recently Wolf[11] has used the copper-catalyzed coupling of ethynyltributyltin detivatives and ruthenium chlorides to form ruthenium oligothienylacetylide complexes. In this latter case, although the highly toxic trimethyltin derivatives have been replaced by much less hazardous tributyltin derivatives, the synthesis of pure terminal alkynes precursors is still necessary.

Within this field we have recently proposed a new use of the Stille[12] reaction, consisting of an original one-pot route straightforwardly leading from aromatic halides to the corresponding ethynyltributyltin aromatic derivatives and, further, to their direct use to form polyacetylenes and polymetallaacetylenes. This novel approach to highly ethynylated materials has been named the extended one-pot (EOP) procedure.[13] In Scheme 1 two EOP pathways (path a_1 and path a_2) are outlined, respectively leading to poly(arylene ethynylene) copolymers $[-C{\equiv}C{-}Ar{-}C{\equiv}C{-}Ar'-]_n$ (path a_1) or poly(metalla ethynylene)(arylene ethynylene) copolymers $[-C{\equiv}C{-}M{-}C{\equiv}C{-}Ar-]_n$ (path a_2).

Both EOP procedures (path a_1 and path a_2) consist of three straightforward steps which are consecutively carried out in the same reaction pot, just by sequentially

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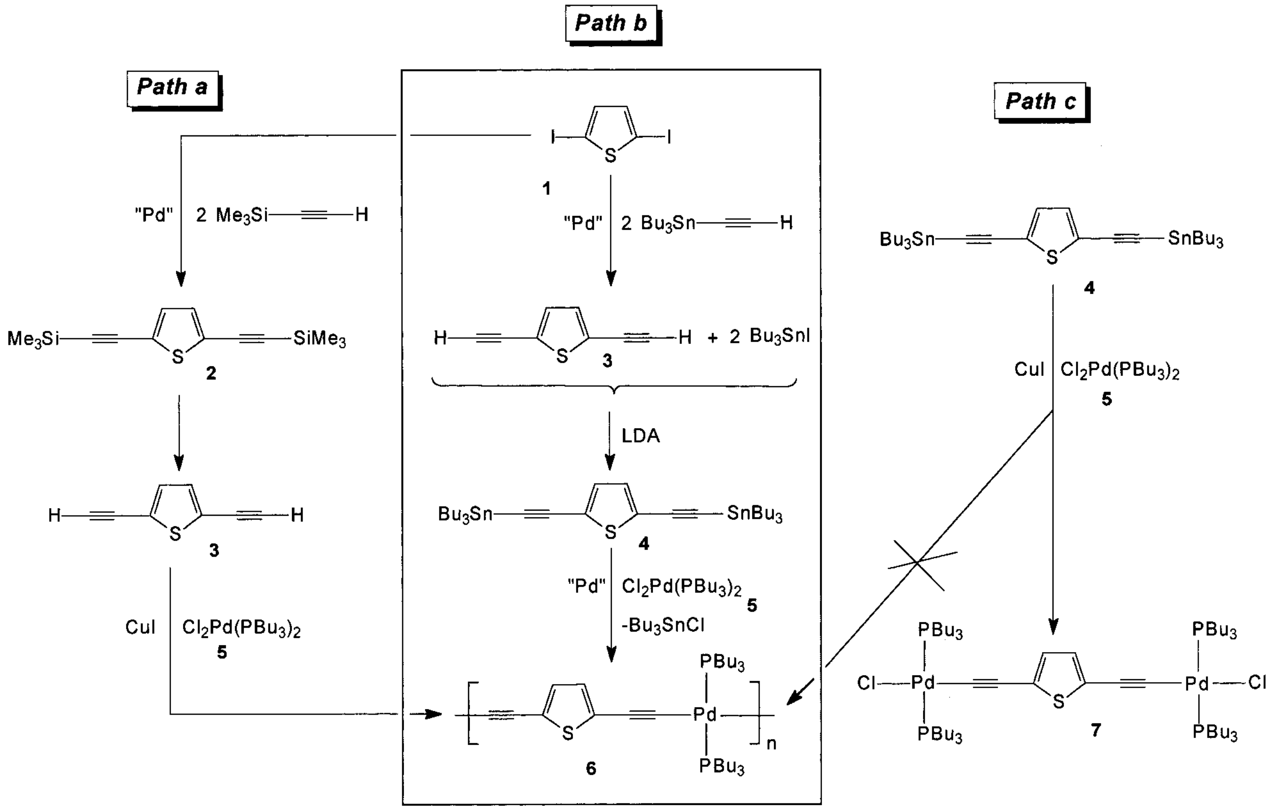
Scheme 2



adding reactants up to the formation of the polymeric product.

In the first step, a diiodoaromatic compound (I−Ar−I) is reacted in THF solvent with 2 equiv of tributyl(ethynyl)tin ($Bu_3Sn-C\equiv C-H$) in the presence of zerovalent palladium. In this reaction the bisethynylaromatic compound ($H-C\equiv C-Ar-C\equiv C-H$) is formed along with 2 equiv of Bu_3SnI side product. To this mixture, cooled to −20 °C, 2 equiv of LDA is added, causing deprotonation of the terminal acetylenic functionalities and their recombination with the Bu_3SnI side product to form the corresponding tin acetylides ($Bu_3Sn-C\equiv C-Ar-C\equiv C-SnBu_3$). Following this transformation, alternatively a second diiodoaromatic compound (I−Ar′−I) (path a_1) or a metal diiodide compound (I−M−I) (path a_2) is added to the reaction mixture; these reaction conditions still are suitable to perform a second palladium-promoted carbon−carbon coupling or a palladium-promoted metal−carbon coupling to afford the corresponding poly(arylene ethynylene) copolymers $[-C\equiv C-Ar-C\equiv C-Ar'-]_n$ (path a_1) or poly(metalla ethynylene)(arylene ethynylene) copolymers $[-C\equiv C-M-C\equiv C-Ar-]_n$ (path a_2). At the end of the overall process, not only is the polymeric material isolated by simple precipitation and washing with methanol, but from the filtrate, the Bu_3SnI side product may be recovered by distillation and reused, thus allowing a recycling of the tin reagent.[13c]

In this work we report on different uses of our extended one-pot (EOP) procedure (i) to conveniently access ethynylthiophene and oligoethynylthiophene derivatives and their subsequent uses to prepare organometallic oligomers by classical routes and (ii) to prepare organometallic polymers by straightforward formation and insertion of ethynylthiophene and oligoethynylthiophene spacers into the polymer backbone. The different synthetic approaches are compared and discussed.

Results and Discussion

Formation of *trans*-bis(tri-*n*-butylphosphine)-μ-[2,5-bis(ethynyl)thiophene]palladium oligomer (6). In Scheme 2 are represented the three complementary synthetic approaches (path a, path b, and path c) that we performed in order to prepare the *trans*-bis(tri-*n*-butylphosphine)-μ-[2,5-bis(ethynyl)thiophene]palladium oligomer (**6**).

Path a represents the classical synthetic route[5] to access transition metal σ-acetylide complexes and polymers, consisting of the (i) Pd-catalyzed TMSA−diiodide coupling, (ii) TMS deprotection, and (iii) copper-catalyzed dehydrohalogenation. In this route both the TMS intermediate (**2**) and the terminal alkyne intermediate (**3**) need to be isolated and purified before their use in the subsequent step. The Pd-catalyzed TMSA−2,5-diiodothiophene coupling to obtain the bis[(trimethylsilyl)ethynyl]thiophene (**2**) was performed introducing some modifications to the procedure described by Whitesides[6a] and Raithby,[14] consisting of the use of an ultrasound bath to break up the solid mass formed in the flask during the reaction and the use of sublimation instead of chromatographic separation to isolate the final product. These modifications conveniently allowed isolation of **2** in 96% yield. Formation of **3** was accomplished by treatment of **2** under standard desilylation conditions,[6a] and after workup, pure **3** was isolated

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by Kugelrohr distillation. The pure product, isolated as a colorless liquid, is a quite sensitive and hazardous material[6a] that became dark upon standing.[14] However if stored under argon at −20 °C in sealed vials, it crystallizes and remains indefinitely stable. Reaction of **3** with *trans*-dichlorobis(tri-*n*-butylphosphine)palladium (**5**) was performed under standard dehydrohalogenation conditions.[5] Reactants were dissolved in diethylamine and stirred at 50 °C in the presence of CuI. The progress of the reaction was periodically checked by ^{13}P NMR.[15] When variations no longer were observed in the ^{13}P NMR spectrum (15 h), the solution was filtered and concentrated to a minimum volume. Addition of methanol caused precipitation of a red-brown material, which was filtered, washed with methanol, and dried under vacuum. Subsequent chromatographic purification and characterization showed that the product resulted from coupling of **3** and **5** (vide infra).

Starting from the same diiodide (**1**), the EOP route (path b) was started with the reaction of **1** with tributyl(ethynyl)tin in THF at 70 °C in the presence of 0.1% of Pd(PPh$_3$)$_4$. After overnight stirring, a sample of the reaction mixture examined by ^{1}H NMR[16] showed quantitative transformation into 2,5-bis(ethynyl)thiophene (**3**) and tributyltin iodide side product. The reaction mixture was then cooled at −20 °C, and lithium diisopropylamide (LDA) was added. The addition of the base provoked deprotonation of the alkyne and its recombination with the tin halide, to form the 2,5-bis[(tributyltin)ethynyl]thiophene (**4**). Also this transformation was clearly evidenced by ^{1}H NMR analysis[16] of a sample of the reaction mixture. To this mixture was added *trans*-dichlorobis(tri-*n*-butylphosphine)palladium (**5**), and the reaction flask was maintained for an additional 24 h at 70 °C. After cooling and vacuum evaporation to a minimum volume, addition of methanol caused precipitation of a red-brown material. This residue when treated with THF, CH$_2$Cl$_2$, or CHCl$_3$ leaves some insoluble material.[17] The soluble part, purified by column chromatography, proved to be the product of coupling of **4** and **5** (vide infra).

From the filtrate, after evaporation of volatiles and vacuum distillation of the oily residue, it was possible to recover most of the Bu$_3$SnCl formed as side product.

Path c has been performed according to the procedure used by Wolf[11] consisting of the copper-catalyzed coupling of ethynyltributyltin detivatives and metal chlorides. Although this route has been used only to form ruthenium oligothienylacetylides, we decided to try it for the formation of polymeric materials of type **6** since the use of tributyltin derivatives presents lesser environmental and safety concerns[10] than the use of trimethyltin derivatives as in the case of Lewis' method. In this synthetic route it is not possible to take advantage of the EOP procedure to form the 2,5-bis[(tributyltin)ethynyl]thiophene (**4**) (first part of path b), since the unavoidable[18] residual presence of palladium catalyst (from the first step of path b) would mask the possible copper catalysis in path c. As a consequence, to cleanly perform path c, **4** must be prepared in a pure form[19] by the reaction of pure **3** and Et$_2$NSnBu$_3$. Reaction of **4** and **5** was carried out in refluxing chlorobenzene in the presence of 10% CuI. After 15 h a sample of the reaction mixture[14] examined by ^{13}P NMR showed only the presence of a broad peak at 11 ppm. After cooling, filtration, and evaporation to a minimum volume, addition of methanol caused the formation of a dark precipitate, which after workup was identified as the bimetallic complex **7**.

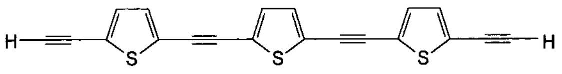

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Figure 1

Formation of the [2-(Ethynyl)thiophene]-2,5-bisethynylthiophene Spacer (13). The introduction of different types of organic spacers in organometallic conjugated polymers should result in a different degree of electronic communication between metal centers and consequently in the tuning of related properties manifested by these materials. In this respect we studied suitable routes to form and then to connect the oligoethynylthiophene **13** (Figure 1) with the bis(tri-*n*-butylphosphine)palladium moieties.

Two different one-pot routes (path a and path b of Scheme 3) have been performed in order to prepare precursors **9** and **11**, which, after further transformations, will be used in the EOP and Hagihara synthetic protocols, respectively, to connect the oligoethynylthiophene spacer **12** to the palladium unit.

Preparation of **9** and **11** have in common with Scheme 2 the first two steps leading from 2,5-diiodothiophene (**1**) to 2,5-bis[(tributyltin)ethynyl]thiophene (**4**). In the present case, following formation of **4**, 2-iodothiophene (**8**) or alternatively 2-iodo-5-(trimethylsilyl)thiophene (**10**) was directly added to the same reaction mixture where **4** was formed, and after 24 h of further warming at 70 °C, **9** and **11** were formed, respectively.

As in the case of the EOP route to form **6** (path b of Scheme 2), each step of transformations of path a and path b can be conveniently monitored by ^{1}H NMR spectroscopy.

Adopting the procedure described by Wakefield,[20] treatment of 2,5-bis(2-thienylethynyl)thiophene (**9**) with *sec*-BuLi in the presence of TMDA and I$_2$ afforded 2,5-[2,2′-(5,5′-diiodo)bisthienyl]bisethynylthiophene (**12**) (eq 1), a material suitable for use in the EOP protocol to be linked to metal moieties. Under different reaction conditions Cava and co-workers have attempted conversion of **9** into **12** by the action of *n*-BuLi and I$_2$. However

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[15] A sample of the reaction mixture (0.4 mL) was loaded in a 5 mm NMR tube. To this a little amount of C$_6$D$_6$ (0.1 mL) was added for lock purpose.

[16] The sequential check of the transformation progresses was typically performed by withdrawing a sample of the reaction mixture (0.1−0.2 mL), stripping off the solvent under reduced pressure (10−15 mmHg/25 °C, 20 min), redissolution with CDCl$_3$, and recording the ^{1}H NMR spectrum. It is recommended not to use a vacuum oil pump to dry samples since Bu$_3$SnC≡CH is volatile enough to be lost under these condition, thus obtaining wrong information on completion of step 1.

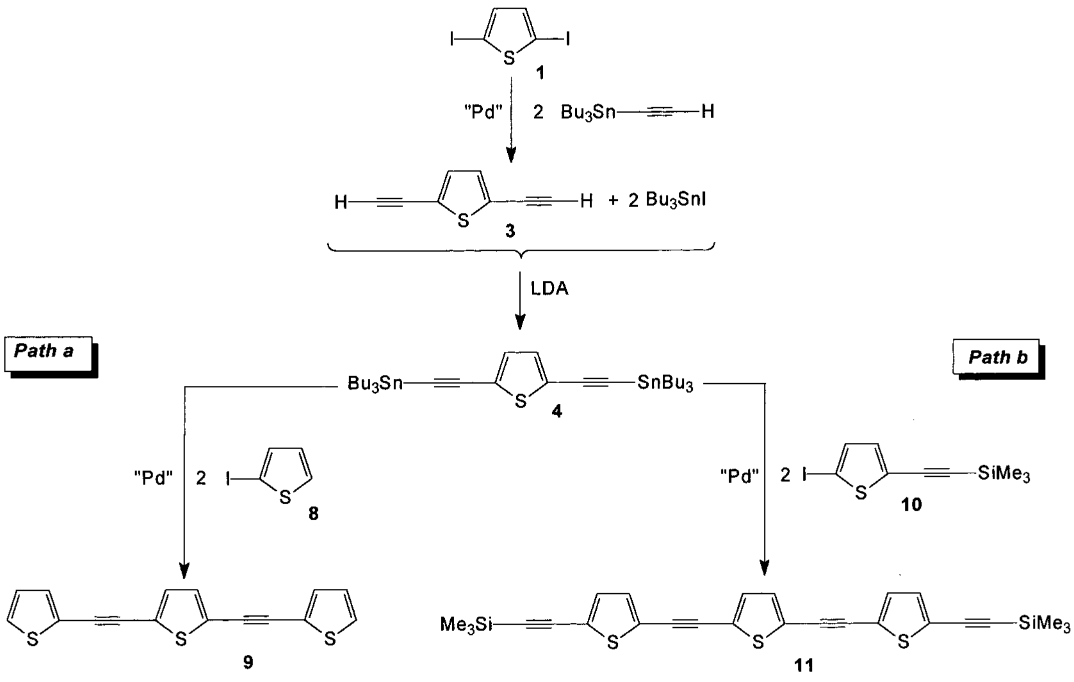
[17] Formation of insoluble material might be related to the formation of insoluble higher-order polymers.

[18] 2,5-Bis[(tributyltin)ethynyl]thiophene (**4**) is a high-boiling oily material whose purification is very difficult. Attempts of performing vacuum distillation lead to thermal decomposition; chromatographic separation partially cleaves tributyltin groups.

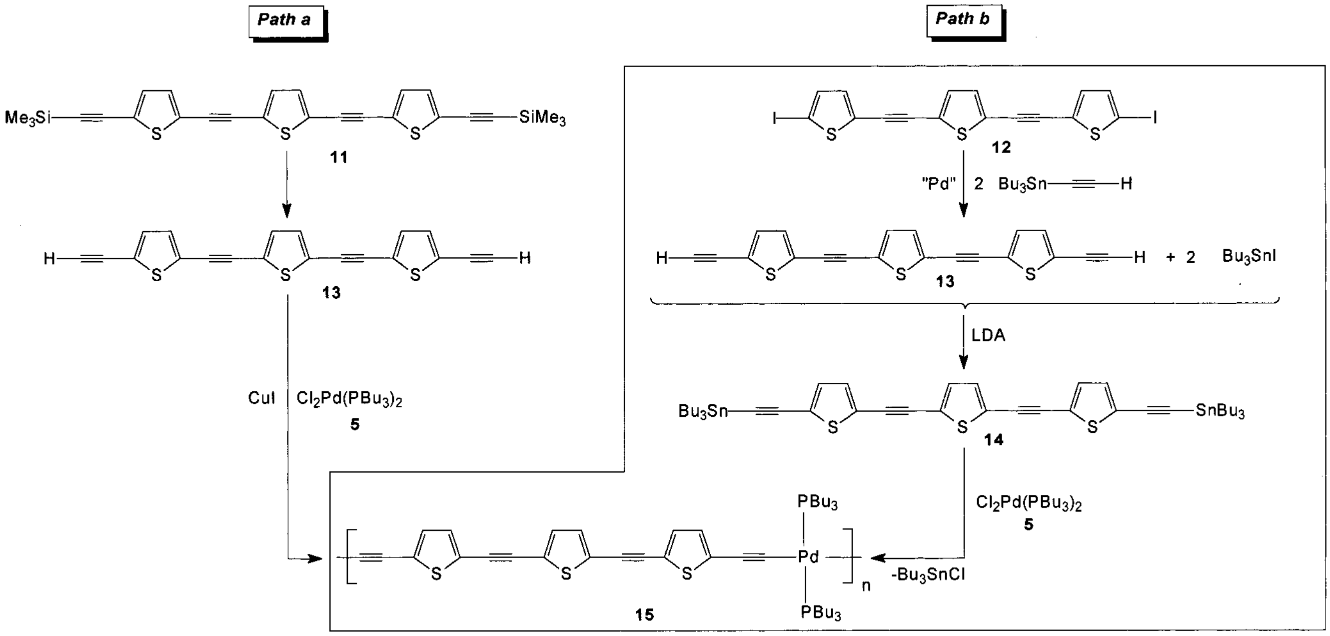
[19] Viola, E.; Lo Sterzo C.; Crescenzi, R.; Frachey, G., *J. Organomet. Chem.* **1995**, *493*, C9.

[20] Wakefield, B. J. *Organolithium Methods*; Academic Press: London, 1988.

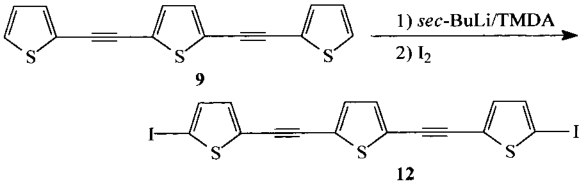
Scheme 3



Scheme 4



they reported[21] that under their conditions an inseparable mixture of **12** and the corresponding monoiodo derivative is obtained.



(1)

Formation of *trans*-bis(tri-*n*-butylphosphine)-*μ*-[2,2′-bis(ethynyl)thiophene]-2,5-bisethynylthiophene]palladium Polymer (15). The synthesis of the oligoethynylthiophene spacers **11** and **12** allowed a complementary approach to the formation of the organometallic species **15**. In Scheme 4 are represented (i) the classical TMS deprotection/CuI-catalyzed dehydrohalogenation sequence (path a) and (ii) the EOP route (path b), both leading to the *trans*-bis(tri-*n*-butylphosphine)-*μ*-[2,2′-bis(ethynyl)thiophene]-2,5-bisethynylthiophene]palladium oligomer (**15**).

Path a starts with removal of the protecting trimethylsilyl groups on **11**. With respect to the standard procedure,[6a] since **11** is insoluble in methanol, the desilylation reaction was carried out in a 1:1 THF/MeOH mixture in the presence of a small amount of an aqueous KOH solution. Following workup and chromatographic

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[21] Tormos, G. V.; Nugara, P. N.; Lakshmikantham, M. V.; Cava, M. P. *Synth. Met.* **1993**, *53*, 271

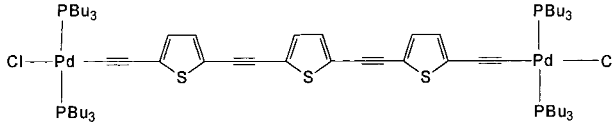

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Figure 2

separation, pure **13** was isolated in 67% yield as a yellow oil, which showed to be quite unstable, turning dark upon standing. Because of its sensitivity, this compound was used immediately after its preparation. In the subsequent step, **13** was reacted with *trans*-dichlorobis(tri-*n*-butylphosphine)palladium (**5**) under typical Hagihara[5] conditions. However, using diethylamine as solvent and in the presence of a catalytic amount of CuI, the dehydohalogenation route afforded a mixture of products, which after chromatographic separation were identified as being short oligomers of type **15** (vide infra) and the bimetallic complex **16** (Figure 2).

Path b was performed under the same conditions previously used for the formation of polymer **6** (Scheme 2). The Stille coupling of **12** with tributyl(ethynyl)tin in refluxing THF in the presence of $Pd(PPh_3)_4$ afforded [2-(ethynyl)thiophene]-2,5-bisethynylthiophene (**13**) and tributyltin iodide as side product. Upon cooling at −20 °C, addition of LDA to this mixture caused deprotonation of the alkyne and its recombination with the tin halide to form [2-tributyltin(ethynyl)thiophene]-2,5-bisethynylthiophene (**14**). To this mixture *trans*-dichlorobis(tri-*n*-butylphosphine)palladium (**5**) was subsequently added, and the reaction mixture was warmed to reflux for an additional 24 h. After cooling, precipitation, and washing with methanol, a red-brown powder was isolated. Evaporation of the filtrate and vacuum distillation of the oily residue allowed almost complete recovery of the Bu_3SnI side product. The red-brown material consisting of **15** upon treatment with THF, CH_2Cl_2, or $CHCl_3$ left some insoluble residue.[17] The soluble part analyzed by GPC proved to be the product of coupling of **14** and **5** (vide infra).

Characterization of the Products. Materials obtained as a result of the coupling between the ethynyl thiophene spacers **3** and **13** with *trans*-dichlorobis(tri-*n*-butylphosphine)palladium (**5**), using the different synthetic approaches, have been characterized by gel permeation chromatography and NMR spectroscopy. In Table 1 are reported molecular weight, molecular weight distribution, and degree of polymerization of the different materials estimated using the GPC techniques (relative to polystyrene standard); also given is the degree of polymerization as estimated by ^{31}P NMR spectroscopy, by measure of internal vs terminal relative intensities of phosphorus signals. It is important to note that with the use of the EOP procedure in the case of formation of both **6** and **15**, after precipitation, part of the isolated material remained insoluble[17] (entries 2, 4). In the formation of polymer **6** (entries 1, 2), besides yields, only slight differences were found between the characteristics of materials obtained from the two different procedures (paths a and b of Scheme 2). In both cases, only short oligomers were obtained. The situation is slightly different in the case of formation of **15** (entries 3 and 4). Using the dehydrohalogenation procedure an appreciable amount (37%) of the bimetallic compound **16** accompanies the formation of short oligomers, while the EOP procedure affords slightly higher oligomers. It is remarkable that the value of the degree of polymerization as estimated by ^{31}P NMR is in substantial agreement with the value of the polymerization degree as estimated by GPC.[22]

The fact that independently of the different adopted procedures, in the case of formation of either polymer **6** and **15**, only short-term oligomers were obtained is indicative of the general difficulties encountered in the formation of palladium-based metallapolyynes.[24] In this respect it may be of significance that the palladium-based species are the most rarely reported. Despite this limitation, because of their intrinsic value, we maintained our interest in oligomeric materials of type **6** and **15**. This confidence is based on the fact that for conjugated polymers electronic and photoactive properties are little related to polymer chain length, since these properties rapidly tend to saturation with the increase of chain length.[23b,25] As a confirmation of this, preliminary results obtained using oligomeric material of type **15**, as obtained in the present work, have shown an excellent behavior when used for the fabrication of sensitive membranes for gas and vapor detection.[26]

Recovery and Recycling of Tin, a Fully Integrated Process. The organometallic materials **6** and **15** formed by the EOP routes outlined in path b of Schemes 2 and 4 were isolated and purified by precipitation and repeated washings with methanol. In addition to the polymeric product we also obtained a methanolic rinsing solution containing the reaction solvent, lower oligomers, residual phosphine ligand, and the Bu_3SnCl side product. From this solution, upon evaporation of the volatiles, a dark, viscous residue remained, from which it was possible to recover up to 92% of pure Bu_3SnCl by vacuum distillation. The recovered Bu_3SnCl was subsequently utilized in the reaction with the lithium acetylide ethylenediamine complex to form new $Bu_3SnC{\equiv}CH$[27] (eq 2), which is the coupling partner of the thiophene derivatives **1** and **12** at the beginning of the three EOP processes outlined in Scheme 3 and path b of Schemes 2 and 4.

$$Bu_3SnCl + H{-}C{\equiv}C^-\,Li^+ \longrightarrow Bu_3Sn{-}C{\equiv}C{-}H \qquad (2)$$

The possibility of using the Bu_3SnCl recovered at the end of the polymerization process to form new $Bu_3SnC{\equiv}$

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(22) Evidently, polymetallaacetylene polymers are a special class of rodlike polymers. Thus, factors that are generally limiting the reliability of polystyrene calibration in the use of the GPC technique for the determination of molecular weights of organic rodlike polymers[6a,23] in this case are balanced by other effects.

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Table 1. Yields and Molecular Weights for Polymers 6 and 15 Obtained with Different Procedures[a]

		yield (%)	M_w[b]	M_n[c]	MWD[d]	DP(M_w)[e]	DP(M_n)[f]	DP(NMR)[g]
6	(1) dehydrohalogenation	57	3000	1300	2.3	5	2	3
	(2) extended one pot (EOP)	76	2750	1700	1.6	4	3	5
14	(3) dehydrohalogenation	60	2200	1000	2.2	3	1	3
	(4) extended one pot (EOP)	73	4000	1500	2.6	5	2	6

[a] Calculated on the soluble part of the polymeric material. [b] Weight-average molecular weights. [c] Number-average molecular weights. [d] Molecular weight distribution (M_w/M_n). [e] Degree of polymerization; calculated on the basis of the M_w value. [f] Degree of polymerization; calculated on the basis of the M_n value. [g] Degree of polymerization; calculated by ^{31}P NMR on the basis of internal vs terminal relative intensities of phosphorous signals.

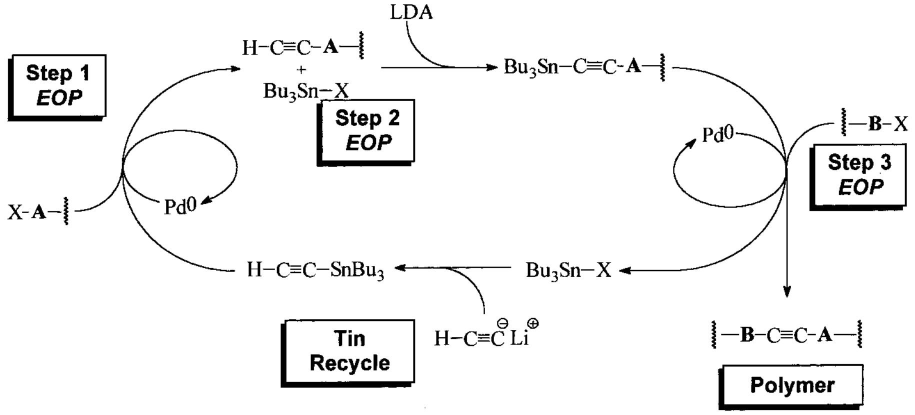

Figure 3

CH allows us to reintroduce the tributyltin moiety into the polymerization process. Figure 3 represents the fully integrated process composed by the three steps of the EOP procedure (steps 1–3) and the recovery and recycle of tin.

A key aspect of the process depicted in Figure 6 is recycling of the tin reagent, which overcomes a major drawback of the Stille reaction, that is, the environmental concern related with the use of toxic and costly organostannanes.[10] In this respect we believe that the present work is in accord not only with the desirability of Stille protocols catalytic in tin[28] but also with the "atom economy" concept recently developed by Trost[29] and the design of environmentally benign chemical processes.[30]

Experimental Section

FT-IR and far-IR spectra were recorded as Nujol mulls, liquids, or casted films on a Fourier Transform Perkin-Elmer 1720 spectrometer. ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR were recorded on a Bruker AC300P spectrometer at 300, 75, and 121.5 MHz, respectively. The ^{1}H NMR chemical shifts are reported in ppm downfield vs Me_4Si, assigning the residual ^{1}H NMR impurity signal in the solvent ($CDCl_3$) to the resonance at 7.24 ppm. The ^{13}C NMR chemical shifts are referenced to the ^{13}C triplet of $CDCl_3$ at 77.00 ppm. ^{31}P NMR spectra were referenced to external 85% H_3PO_4. Molecular weights of the materials were determined with a Perkin-Elmer GPC-HPLC instrument with a UV detector, using a Perkin-Elmer PL gel 10μ mixed N. 0258-2135 column, using $CHCl_3$ and THF as eluent and polystyrene as a standard. Solvents, including those used for NMR and chromatography, and all other liquids were thoroughly degassed before use. Chromatographic separations were performed with 70–230 mesh silica gel. Elemental analyses were performed at the Dipartimento di Chimica of the Università di Roma "La Sapienza".

Standard techniques, with Schlenk type equipment for the manipulation of air-sensitive compounds under argon atmosphere, were employed. All solvents were dried (sodium–potassium alloy for tetrahydrofuran and diethyl ether and Na for the hexanes and amines) and argon-satured prior to use. The compounds *trans*-bis(tributylphosphine)palladium(II) chloride[31] (**5**), 2-iodo-5-[(trimethylsylyl)ethynyl]thiophene[32] (**9**), 2,5-bis[(tributylstannyl)ethynyl]thiophene[19] (**4**), and bis(acetonitrile)-palladium(II) chloride[33] were prepared by reported procedures. Other chemicals were purchased from Aldrich or Strem and used as received unless otherwise specified.

Preparation of 2,5-[(Trimethylsilyl)ethynyl]thiophene (2). To a mixture of 2,5-diiodothiophene (**1**) (12.01 g, 49.65 mmol), $(CH_3CO_2)_2Cu$ (0.5 g, 2.75 mmol), $PdCl_2(CH_3CN)_2$ (1.05 g, 4.05 mmmol), and triphenylphosphine (1.48 g, 5.64 mmol) in diisopropylamine (50 mL) was added dropwise trimethylsilylacetylene (13.21 g, 134.5 mmol) during 1 h under stirring at room temperature. The reaction mixture was then refluxed for 3 h. During this time the color of the reaction mixture changed from light green to black, and most of the initial slurry changed to a solid mass. From time to time immersion into an ultrasound bath helped to break up the solid mass. After cooling, the precipitated ammonium iodide was filtered off and washed with dichloromethane (2 × 50 mL). The combined filtrates were treated with a 5% acqueous solution of HCl (2 × 50 mL), then with water (3 × 50 mL), and dried over magnesium sulfate. After addition of Celite, the solvent was evaporated under reduced pressure and the residue was sublimed at 90 °C and 10^{-2} Torr, cooling the coldfinger at −10 °C. In the event of the presence of a little amount of

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contaminating bis(trimethylsilyl)butadiyne, this side product can be eliminate by collecting and discarding the first amount of the sublimate. The product (13.15 g, 96%) was isolated as white solid. ^{1}H NMR ($CDCl_3$ ppm): 7.02 (s, 2H), 0.23 (s, 18H). IR (Nujol): 2147 (s), 1250 (s), 1173 (s), 845 (s) cm^{-1}. Spectroscopic data are in agreement with literature reports.[6a,14]

Preparation of 2,5-Bis(ethynyl)thiophene (3). To a solution of 2,5-[(trimethylsilyl)ethynyl]thiophene (**2**) (0.49 g, 1.77 mmol) in degassed methanol (30 mL) was added 0.1 mL of a 0.5 M solution (0.05 mmol) of KOH in water. The solution was stirred at room temperature for 1 h, then diluted with water (50 mL), and extracted with pentane (3 × 30 mL). The combined organic layers were dried over sodium sulfate, and after filtration, the solvent was removed under reduced pressure at room temperature. The liquid residue was purified by Kugelrohr distillation (40 °C, 2×10^{-1} mbar) to give 0.20 g (86%) of product as a colorless oil. Pure **3** if left standing in air at room temperature rapidly turns dark. However, if stored under argon in sealed vials at −20 °C it crystallizes and remains indefinitely stable. ^{1}H NMR ($CDCl_3$ ppm): 7.09 (s, 2H), 3.32 (s 2H). IR (liquid): 2106 (m), 1214 (s), 1209 (m), 808 (s) cm^{-1}. Spectroscopic data are in agreement with literature reports.[6a,14]

Preparation of Poly{2,5-bis(ethynyl)thiophenebis(tributylphosphine)palladium} (6). Path a: Dehydrohalogenation Route. 2,5-Bis(ethynyl)thiophene (**3**) (0.13 g, 0.98 mmol) was dissolved in 20 mL of diethylamine, and to this solution *trans*-$Cl_2Pd\ (PBu_3)_2$ (**5**) (0.57 g, 0.98 mmol), followed by CuI (5 mg), was added. After 15 h of stirring at room temperature the reaction mixture was filtered on a glass frit covered with Celite and reduced to a minimum volume by evaporation under vacuum. Upon addition of methanol to the filtrate, a red-brown solid precipitated, which was collected on a glass frit and washed with methanol. The residue was redissolved in a minimum amount of dichloromethane and purified chromatographically using a silica gel column and toluene as the eluent. Removal of the solvent left 0.4 g (57%) of product as a red-brown solid. ^{1}H NMR ($CDCl_3$ ppm): 6.56 (s, 2H, *thiophene*), 2.1−0.86 (m, 54H, P*Bu*$_3$). ^{13}C NMR ($CDCl_3$ ppm): 127.0, 116.9 (*thiophene*), 105.7, 97.5 (−*C*≡*C*−), 26.7, 24.61 (m), 13.9 (P*Bu*$_3$). ^{31}P NMR ($CDCl_3$, ppm): 11.39 (*P terminal*), 7.14 (*P internal*). IR (Nujol): 2088 (s) 1510 (m) 394 (w) cm^{-1}. Anal. Calcd for $C_{32}H_{56}P_2PdS$: C, 59.94; H, 8.80. Found: C, 58.98; H, 7.27.

Path b: EOP Route. To a solution of 0.010 g (0.008 mmol) of $Pd(PPh_3)_4$ and 0.147 g (0.43 mmol) of 2,5-diiodothiophene (**1**) in 20 mL of THF was added 0.270 g (0.86 mmol) of tributyl(ethynyl)tin. After overnight stirring at 70 °C, ^{1}H NMR analysis[15] indicated complete consumption of the starting tin reagent with formation of **3** and Bu_3SnI. After cooling to −20 °C, 0.5 mL (10.0 mmol) of a solution of LDA (2.0 M in THF/heptane/ethylbenzene) was added, and the mixture allowed to warm to room temperature. A sample of the reaction mixture examined by ^{1}H NMR analysis[15] indicated complete conversion of the alkyne moieties into the corresponding tributyltinalkynyl functionalities. To this solution was added *trans*-$Cl_2Pd\ (PBu_3)_2$ (**5**) (0.250 g, 0.43 mmol), and the mixture was warmed to reflux. After 24 h ^{1}H NMR analysis[15] indicated complete consumption of reactants; then, after cooling, the mixture was filtered over Celite to eliminate the spent catalyst and the filtrate was evaporated under vacuum to a small volume. Upon addition of methanol, a red-brown solid precipitated, which was collected by filtration, washed repeatedly with methanol, and dried under vacuum. The crude product was purified by chromatography over silica by using toluene as the eluent. The product (0.210 g, 76%) was obtained as a dark solid. Evaporation under reduced pressure of the methanolic rinsing solution afforded a dark oil, which was submitted to vacuum distillation (Kugelrohr, 120 °C/10^{-2} Torr), giving 0.257 g (92%) of tributyltin chloride. Spectroscopic characteristics were identical to those of the material obtained with the dehydrohalogenation route.

Path c: Copper-Catalyzed −C≡C−$SnBu_3$/Cl−Pd Coupling. To a degassed solution of *trans*-$Cl_2Pd\ (PBu_3)_2$ (**5**) (0.202 g, 0.35 mmol) and CuI (6.7 mg, 0.035 mmol) in chlorobenzene (20 mL) was added 2,5-bis[(tributylstannyl)ethynyl]thiophene (**4**) (0.250 g 0.35 mmol). The solution was heated to reflux overnight (15 h) and then cooled to room temperature. The mixture was then filtered through Celite to eliminate the spent catalyst, and the filtrate was reduced under vacuum to a small volume. Addition of methanol precipitated a red-brown solid, which was collected by filtration, washed repeatedly with methanol, and dried under vacuum. The solid was purified chromatographically using a silica gel column and toluene/THF (8:2 v/v) as the eluent. Removal of the solvent under reduced pressure yielded 0.083 g (39%) of product (**7**) as dark solid. ^{1}H NMR ($CDCl_3$ ppm): 6.59 (s, 2H, *thiophene*), 1.91−1.85 (m, 24H, $P(CH_2CH_2C\mathit{H}_2CH_3)_3$) 1.56−1.36 (m, 48H, $P(C\mathit{H}_2C\mathit{H}_2CH_2CH_3)_3$) 0.90 (t, 36H, $J = 7.1$ Hz, $P(CH_2CH_2CH_2C\mathit{H}_3)_3$). ^{13}C NMR ($CDCl_3$ ppm): 127.2, 126.1 (*thiophenes*) 102.0 (t, $J = 14$ Hz, (Pd−*C*≡C−), 98.4 (br, Pd−C≡*C*−), 26.4 ($P(CH_2CH_2\mathit{C}H_2CH_3)_3$ 24.4 (t, $J = 7$ Hz, $P(CH_2\mathit{C}H_2CH_2CH_3)_3$, 22.8 (t, $J = 14$ Hz, $P(\mathit{C}H_2CH_2CH_2CH_3)_3$), 13.8 ($P(CH_2CH_2CH_2\mathit{C}H_3)_3$). ^{31}P NMR ($CDCl_3$, ppm): 10.7. IR (casted film): 2857−2871 (s), 2089 (m) cm^{-1}. Anal. Calcd for $C_{56}H_{110}Cl_2P_4Pd_2S$: C, 61.92; H, 7.09. Found: C, 62.12; H, 7.2.

Preparation of 2,5-(2,2′-Bisthienyl)bisethynylthiophene (9). To a solution of 0.25 g (0.22 mmol) of $Pd(PPh_3)_2$ and 0.92 g (2.68 mmol) of 2,5-diiodothiophene in 50 mL of THF was added 1.69 g (5.4 mmol) of ethynyltributyltin. After overnight stirring at 70 °C, ^{1}H NMR analysis[15] indicated complete consumption of the starting tin reagent with formation of **3** and Bu_3SnI. After cooling to −20 °C, 3.5 mL (7.02 mmol) of a solution of LDA (2.0 M in THF/heptane/ethylbenzene) was added and the mixture allowed to warm to room temperature. A sample of the reaction mixture examined by ^{1}H NMR analysis[15] indicated complete conversion of the alkyne moieties into the corresponding tributyltinalkynyl functionalities. To this solution was added 1.13 g (5.4 mmol) of 2-iodothiophene (**8**), and the mixture was warmed to reflux. After 24 h ^{1}H NMR analysis[15] indicated complete consumption of reactants and formation of **9**. After cooling, the solvent was evaporated under reduced pressure and 50 mL of diethyl ether was added to the reaction mixture, followed by the addition of 100 mL of a 50% solution of KF in water. The mixture was rapidly stirred for 30 min while argon was bubbled through the solution and then transferred into a separatory funnel. The ether solution was washed with water (3 × 50 mL), dried over magnesium sulfate, and filtered. Celite (10 g) was added to the filtrate, and the mixture was evaporated to dryness in vacuo. The residue was chromatographed on silica gel using hexanes as the eluent to yield 0.41 g (1.39 mmol, 52%) of a pale yellow powder. An analytical sample was obtained by sublimation at 95 °C/4.5×10^{-6} mbar, cooling the coldfinger at −10 °C. ^{1}H NMR ($CDCl_3$ ppm): 7.01 (m, 2H $J = 5$ Hz, $J = 3.8$ Hz), 7.13 (s, 2H) 7.28 (m, 2H, $J = 1.0$ Hz, $J = 5$ Hz) 7.31 (m, 2H $J = 1.0$ Hz, $J = 5.0$ Hz). IR (casted film): 3104 (w), 2197 (w), 1410 (w), 1195 (s), 699 (s) cm^{-1}. Spectroscopic data are in agreement with literature reports.[21]

Preparation of [2-Trimethylsilylethynylthiophene]-2,5-bis(ethynyl)thiophene (11). To a solution of 0.21 g (0.19 mmol) of $Pd(PPh_3)_2$ and 0.78 g (2.28 mmol) of 2,5-diiodothiophene in 50 mL of THF was added 1.43 g (4.6 mmol) of ethynyltributyltin. After overnight stirring at 70 °C, ^{1}H NMR analysis[15] indicated complete consumption of the starting tin reagent with formation of **3** and Bu_3SnI. After cooling to −20 °C, 3.0 mL (6.0 mmol) of a solution of LDA (2.0 M in THF/heptane/ethylbenzene) was added, and the mixture allowed to warm to room temperature. A sample of the reaction mixture examined by ^{1}H NMR analysis[15] indicated complete conversion of the alkyne moieties into the corresponding tributyltinalkynyl functionalities. To this solution was added 1.40 g (4.6 mmol) of 2-iodo-5-[(trimethylsilyl)ethynyl]thiophene (**10**), and the mixture was warmed to reflux. After 24 h ^{1}H NMR analysis[15] indicated complete consumption of reactants and formation of **11**. After cooling, the solvent was evaporated under reduced pressure, and 50 mL of diethyl ether was added to the reaction mixture, followed by the addition of 100 mL of a 50% solution of KF in water. The mixture was rapidly stirred for 30 min while argon was bubbled through the solution and then transferred into a separatory funnel. The ether solution was washed with water (3 × 50 mL), dried over magnesium sulfate, and filtered. Celite (10 g) was added to the filtrate, and the mixture was evaporated to dryness in vacuo. The residue was chromatographed on a silica gel column packed with hexanes using a gradient elution first with hexanes and then with a mixture of hexanes/CH_2Cl_2 (95:5 v/v). Evaporation of the solvent yielded 0.67 g (60%) of **11** as a pale yellow powder. ^{1}H NMR ($CDCl_3$ ppm): 7.09 (s, 4H), 7.14 (s, 2H) 0.23 (s, 18H). IR (casted film): 2963−2852 (m), 2143 (m), 1415 (w), 1202 (s), 801 (s) cm^{-1}. Spectroscopic data are in agreement with literature reports.[34]

Preparation of 2,5-[2,2′-(5,5′-Diiodo)bisthienyl]bisethynylthiophene (12). A flask was charged with 0.41 g (3.5 mmol) of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), 0.52 g (1.8 mmol) of 2,5-(2,2′-dithienyl)diethynylthiophene (**9**), and 50 mL of hexane. To this solution was added 2.7 mL (3.5 mmol) of *sec*-BuLi (1.3 M in cyclohexane) by syringe, and the reaction mixture was refluxed for 30 min. After this time the reaction mixture was left to reach room temperature and then was cooled to 0 °C. I_2 (0.9 g, 3.5 mmol) was added and the mixture stirred at room temperature for 30 min. To the reaction mixture was then added water (100 mL), and the mixture was extracted with benzene (3 × 50 mL). The organic layer was further washed with water (4 × 100 mL), dried over sodium sulfate, and filtered. Celite was added to the filtrate, and after removal of the solvent, the coated product was chromatographed on silica gel (hexane) to yield 0.31 g (40%) of the product, which was recrystallized from EtOH. ^{1}H NMR ($CDCl_3$ ppm): 7.13 (d, $J = 3.8$ Hz, 2H), 6.92 (d, $J = 3.8$ Hz, 2H) 7.13 (s, 1H). ^{13}C NMR ($CDCl_3$ ppm): 137.2, 133.7, 132.5, 128.5, 124.4, 75.8 (*thiophene*), 87.6, 86.4 ($C{\equiv}C$). IR (Nujol): 2193 (w), 1190 (m), 799 (s), 501 (s) cm^{-1}. Anal. Calcd for $C_{16}H_6S_3I_2$: C, 35.06; H, 1.10. Found: C, 35.5; H, 1.15.

Preparation of [2-Ethynylthiophene]-2,5-bisethynylthiophene (13). This compound was prepared with the same procedure used for 2,5-bis(ethynyl)thiophene (**3**) by treating 0.29 g (0.61 mmol) of [2-trimethylsilylethynylthiophene]-2,5-bis(ethynyl)thiophene (**11**), dissolved in a mixture of THF and MeOH (1:1), with 0.5 mL of a 0.5 M solution (0.25 mmol) of KOH in water. The product was isolated by chromatography on a silica gel column using a mixture of hexanes/THF (9:1) as the eluent. Removal of the solvent yielded 0.14 g (0.41 mmol, 67%) of the product as a yellow oil that darkened upon standing. This compound was used immediately after its preparation. ^{1}H NMR ($CDCl_3$ ppm): 7.14 (d, $J = 3.8$ Hz, 2H), 7.11 (d, $J = 3.8$ Hz, 2H), 7.15 (s, 2H), 3.38 (s, 2H). IR (casted film): 3282 (m), 2199 (w), 2098 (w), 1197 (m), 800 (s) cm^{-1}. Spectroscopic data are in agreement with literature reports.[34]

Preparation of Poly{[2-ethynylthiophene]-2,5-bisethynylthiophenebis(tributhylphosphine)palladium} (15). Path a: Dehydrohalogenation Route. [2-Ethynylthiophene]-2,5-bisethynylthiophene (**13**) (0.14 g, 0.41 mmol) was dissolved in 20 mL of diethylamine, and to this solution was added *trans*-Cl_2Pd $(PBu_3)_2$ (**5**) (0.24 g, 0.41 mmol) followed by CuI (5 mg). After 15 h of stirring at room temperature all volatile components were removed under reduced pressure. The resulting residue was redissolved in $CHCl_3$ and chromatographed on a silica gel column using the same solvent as the eluant. First was eluted **16** (0.22 g, 37%), followed by **15** (0.21 g, 60%).

Characterization of 15. ^{1}H NMR ($CDCl_3$ ppm): 6.68−7.09 (m, 6H, thiophenes), 2.06−0.81 (m, 54H, P*Bu*$_3$). ^{31}P NMR ($CDCl_3$, ppm): 11.85 (*P terminal*), 7.41 (*P internal*). IR (casted film): 2182 (w), 2099 (m), 1193 (w), 800 (m), 390 (w) cm^{-1}. Anal. Calcd for $C_{44}H_{60}S_3P_2Pd$: C, 61.92; H, 7.09. Found: C, 61.33; H, 7.56. When a **13**/*trans*-Cl_2Pd $(PBu_3)_2$ molar ratio of 1:2 was used, only the bimetallic complex **16** was formed (73%).

Characterization of 16. ^{1}H NMR ($CDCl_3$ ppm): 7.08 (s, 2H *central thiophene*), 7.05 (d, 2H, $J = 3.7$ Hz *lateral thiophenes*), 6.69 (d, 2H, $J = 3.7$ Hz *lateral thiophenes*), 1.89 (m, 12H, $P(CH_2CH_2CH_2CH_3)_3$), 1.52 (m, 12H, $P(CH_2CH_2CH_2CH_3)_3$), 1.46 (m, 12H, $P(CH_2CH_2CH_2CH_3)_3$, 0.91 (t, 18 H, $J = 7.1$ Hz, $P(CH_2CH_2CH_2CH_3)_3$). ^{13}C NMR ($CDCl_3$ ppm): 132.3, 131.7, 131.1, 127.6, 124.4, 119.1 (*thiophenes*), 106.8 (t, $J = 16$ Hz, ($Pd{-}C{\equiv}C{-}$)) 97.9 (br, $Pd{-}C{\equiv}C{-}$) 88.0, 88.1 (${-}C{\equiv}C{-}$), 26.3 ($P(CH_2CH_2CH_2CH_3)_3$ 24.3 (t, $J = 6.3$ Hz, $P(CH_2CH_2CH_2CH_3)_3$, 22.9 (t, $J = 13.4$ Hz, $P(CH_2CH_2CH_2CH_3)_3$), 13.7 ($P(CH_2CH_2CH_2CH_3)_3$). ^{31}P NMR ($CDCl_3$, ppm): 11.06. IR (casted film): 2857−2871 (s), 2189 (w), 2100 (s), 2099 (m), 1194 (w), 799 (m), 359 (w) cm^{-1}. Anal. Calcd for $C_{68}H_{114}S_3Cl_2P_4Pd_2$: C, 56.90; H, 8.00. Found: C, 56.96; H, 8.13.

Path b*:* EOP Route. To a solution of 0.006 g (0.006 mmol) of $Pd(PPh_3)_4$ and 0.16 g (0.26 mmol) of 2,5-[2,2′-(5,5′-diiodo)-bisthienyl]bisethynylthiophene (**12**) in 40 mL of THF was added 0.18 g (0.54 mmol) of ethynyltributyltin. After overnight stirring at 70 °C, ^{1}H NMR analysis[15] indicated complete consumption of the starting tin reagent with formation of **13** and Bu_3SnI. After cooling to −20 °C, 0.34 mL (0.70 mmol) of a solution of LDA (2.0 M in THF/heptane/ethylbenzene) was added, and the mixture allowed to warm to room temperature. A sample of the reaction mixture examined by ^{1}H NMR analysis[15] indicated complete conversion of the alkyne moieties into the corresponding tributyltinalkynyl functionalities. To this solution was added *trans*-Cl_2Pd $(PBu_3)_2$ (**5**) 0.128 g (0.22 mmol), and the mixture was warmed to reflux. After 24 h, ^{1}H NMR analysis[15] indicated complete consumption of reactants; the mixture was then cooled and filtered over Celite to eliminate the spent catalyst, and the filtrate was reduced under vacuum to a small volume. Addition of methanol caused formation of a precipitate that was collected by filtration, washed repeatedly with methanol, and dried under vacuum. The product (0.2 g, 73%) was isolated as a dark red solid. Evaporation under reduced pressure of the methanolic rinsing solution afforded a dark oil, which was submitted to vacuum distillation (Kugelrohr, 120 °C/10^{-2} mmHg), giving 0.064 g (90%) of tributyltin chloride. Spectroscopic characteristics were identical to those of the material obtained with the dehydrohalogenation route.

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Supporting Information Available: ^{1}H NMR spectra accounting for the sequence of transformations from **1** to **9** and related explanatory text. ^{1}H NMR and ^{13}C NMR spectra of compound **16** and related description. This material is available free of charge via the Internet at http://pubs.acs.org.

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