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Combined Use of Palladium-Catalyzed Carbon−Carbon and Metal−Carbon Bond Formations for the Construction of Poly(metallaacetylide) Tethers

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The reaction between (η^5-C_5H_4I)Fe(CO)$_2$CH$_3$ (**2**) and 2,5-bis[(trimethylstannyl)ethynyl]thiophene in the presence of palladium affords the iron dimer $CH_3(CO)_2Fe(\eta^5\text{-}C_5H_4)C{\equiv}CC{=}CHSCH{=}CC{\equiv}C(\eta^5\text{-}C_5H_4)Fe(CO)_2CH_3$ (**4**), which upon treatment with I$_2$ is transformed to the corresponding diiodide $I(CO)_2Fe(\eta^5\text{-}C_5H_4)C{\equiv}CC{=}CHSCH{=}CC{\equiv}C(\eta^5\text{-}C_5H_4)Fe(CO)_2I$ (**5**). Reaction of the latter, in the presence of palladium, with the (trimethylstannyl)acetylide derivatives $L_nM(\eta^5\text{-}C_5H_4)C{\equiv}CC{=}CHSCH{=}CC{\equiv}CSn(CH_3)_3$ (**9a**, ML$_n$ = W(CO)$_3$CH$_3$, **9b**, ML$_n$ = Re(CO)$_3$) affords the polymetallaacetylide tethers $L_nM(\eta^5\text{-}C_5H_4)C{\equiv}CC{=}CHSCH{=}CC{\equiv}CFe(CO)_2(\eta^5\text{-}C_5H_4)C{\equiv}CC{=}CHSCH{=}CC{\equiv}C(\eta^5\text{-}C_5H_4)(CO)_2FeC{\equiv}CC{=}CHSCH{=}CC{\equiv}C(\eta^5\text{-}C_5H_4)ML_n$ (**10**, ML$_n$ = W(CO)$_3$CH$_3$; **11**, ML$_n$ = Re(CO)$_3$). Trimethyltin derivatives of poly(ethynylthiophene) oligomers have been also prepared and tested for their use as spacers in poly(metallaacetylide) complexes.

Introduction

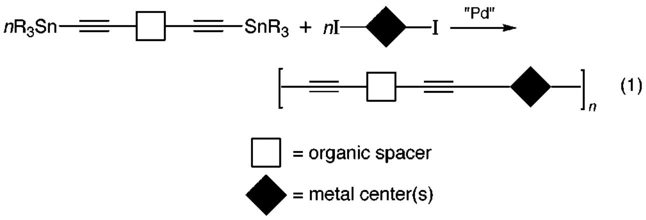
Highly ethynylated organometallic compounds are currently providing new and promising opportunities for the engineering of new materials.[1] Nonlinear optic materials, molecular wires, light harvesting devices, molecular magnets, and liquid crystalline materials are some of the applications for which poly(metallacetylides) may be useful.[2]

The basis for this is *facile* metal-to-ligand charge transfer (MLCT) and the possibility of extended delocalization through the unsaturated chain. These effects can influence physical properties such as polarizability and susceptibility, which can increase by several orders of magnitude compared to those for similar materials not containing transition metals.[2]

Preparative organometallic chemistry provides a way to fine-tune these properties by variation of the organic fragment and/or the type of the metal introduced within the chain.

We have recently disclosed a new route to σ-metallaacetylides based on the ability of palladium to catalyze the formation of metal−carbon bonds.[3] This procedure led to the preparation of a variety of mono- and bis(σ-metallaacetylides) by the coupling of transition-metal iodides to mono- and bis[(trialkylstannyl)acetylides] in the presence of a catalytic amount of palladium.[4,5] This synthetic methodology has proved to be quite general with respect to both the nature of the transition metal involved and the organic functionality supporting the acetylenic moieties (Scheme 1).

Compounds of type **B**−**D** in Scheme 1 are particularly appealing, as they represent multinuclear complexes. Analogous coupling of bis[(trialkylstannyl)acetylides] to bis(metal iodides) instead of *mono*(metal iodides) would constitute an extremely useful and convenient route to the preparation of polymeric materials (eq 1).



(1)

The results of a study of the palladium-catalyzed metal−carbon coupling between (trialkylstannyl)acetyl-

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(1) (a) Irwin, M. J.; Jia, G.; Payne, N. C.; Puddephatt, R. J. *Organometallics* **1996**, *15*, 51. (b) Astruc, D. *Acc. Chem. Res.* **1997**, *30*, 383. (c) Lavastre, O.; Plass, J.; Bachmann, P.; Guesmi, S.; Moinet, C.; Dixneuf, P. H. *Organometallics* **1997**, *16*, 184. (d) Bunz, U. H. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 969. (e) Coat, F.; Lapinte, C. *Organometallics*, **1996**, *15*, 477.

(2) (a) Bruce D. W.; O'Hare, D. *Inorganic Materials*; Wiley: Chichester, England, 1992. (b) Long, N. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 21. (c) Harrimann, A.; Ziessel, R. *Chem. Commun.* **1996**, 1707. (d) Brandy, M.; Weng, W.; Zhou, Y.; Seyler, J. W.; Amoroso, A. J.; Arif, A. M.; Böhme, M.; Frenking, G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 788.

(3) Lo Sterzo, C. *J. Chem. Soc., Dalton Trans.* **1992**, 1989.

(4) (a) Crescenzi, R.; Lo Sterzo, C. *Organometallics*, **1992**, *11*, 4301. (b) Viola, E.; Lo Sterzo, C.; Crescenzi, R.; Frachey, G. *J. Organomet. Chem.* **1995**, *493*, C9. (c) Viola, E.; Lo Sterzo, C.; Crescenzi, R.; Frachey, G. *J. Organomet. Chem.*, **1995**, *493*, 55. (d) Viola, E.; Lo Sterzo, C.; Trezzi, F. *Organometallics* **1996**, *15*, 4352.

(5) (a) Hartbaum, C.; Roth, G.; Fischer, H. *Chem. Ber./Recl.* **1997**, *130*, 479. (b) Hartbaum, C.; Fischer, H. *Chem. Ber./Recl.* **1997**, *130*, 1063.

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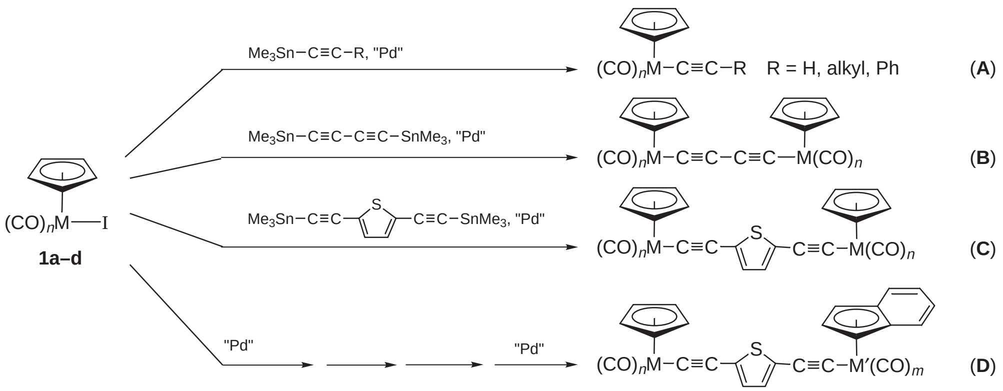
Scheme 1 [a]

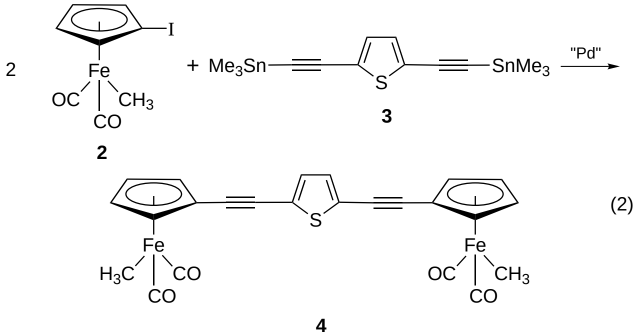


[a] Legend: (**a**) M = Fe, $n = 2$; (**b**) M = Ru, $n = 2$; (**c**) M = Mo, $n = 3$; (**d**) M = W, $n = 3$.

ides and a bis(metal iodide), reported herein, demonstrate the utility of this procedure as a synthetic tool in the preparation of sophisticated poly(metallaacetylide) blocks.

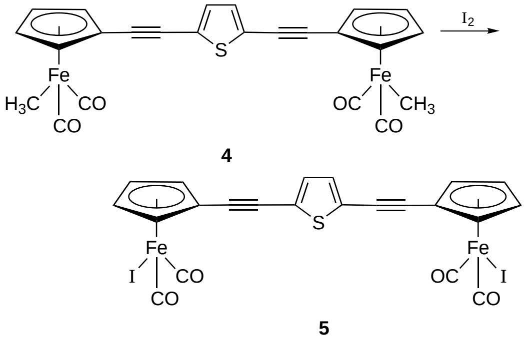
Results and Discussion

The goal we set to prepare poly(metallacetylide) materials via Pd-catalyzed metal−carbon bond formation prompted us to design monomeric molecular units bearing two metal iodide (M−I) moieties. When these compounds are combined with appropiately functionalized tin-acetylides, metallaacetylides of higher order may be constructed. Since it is known that (i) the (η^5-cyclopentadienyl)iodometal carbonyl complexes **1a**−**d** of Scheme 1 can very efficiently be transformed into the corresponding metal σ-acetylides by Pd-catalyzed coupling with trialkyltin acetylides[4] and (ii) the linkage between two cyclopentadienyl rings of (η^5-cyclopentadienyl)metal complexes is synthetically accessible,[6] we decided to bridge two of the latter units by a suitable linker between the cyclopentadienyl rings. The 2,5-bis(ethynyl)thiophene group was chosen both because of the considerable importance of thiophene-based conducting polymers[7] and, more generally, as a model for an unsaturated conjugated system which is essential for electronic communication through metal centers.[1,2] A synthetic procedure previously developed in our group permitted the preparation of acetylene-bridged bis(cyclopentadienyl) dimers.[6] Two equivalents of the (η^5-iodocyclopentadienyl)metal complex **2** with respect to 2,5-bis[(trimethylstannyl)ethynyl]thiophene (**3**) was reacted in the presence of a catalytic amount of palladium catalyst[8] (eq 2). The coupling reaction proceeded smoothly overnight at room temperature, affording the 2,5-diethynylthiophene-bridged bis(cyclopentadienyl) dimer **4** in good yield.



(2)

To use compound **4** in the formation of polymetallic σ-acetylides, the methyl groups on the iron centers needed to be replaced with iodide so that Pd-catalyzed coupling could occur with tin acetylides. Treatment of complex **4** with I_2 in dichloromethane at 0 °C rapidly consumed the starting material; however, the corresponding diiodide **5** (eq 3) was isolated in only 50% yield after column chromatography.



(3)

Next we prepared the acetylide pendant units **9a,b**, to be linked to the Fe−I moieties in **5**. Scheme 2 illustrates the sequence of transformations leading to complexes **9a,b**. The key compound in Scheme 2 is 2-[(trimethylsilyl)ethynyl]-5-[(trimethylstannyl)ethynyl]-thiophene[4d] (**6**), a bis(ethynyl)thiophene derivative bearing a TMS-protected acetylene and a (trimethylstannyl)-acetylene functionality. While under the normal Stille conditions the former is inert,[9] the latter promptly reacts in the presence of a catalytic amount of palladium, with the (η^5-iodocyclopentadienyl)metal complexes **1d,e** to form complexes **7a,b** in 83% and 96%

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(6) (a) Lo Sterzo, C.; Miller, M. M.; Stille, J. K *Organometallics* **1989**, *8*, 2331. (b) Lo Sterzo, C.; Stille, J. K. *Organometallics* **1990**, *9*, 687.

(7) Early references on the use of dichlorobis(acetonitrile)palladium-(II) (Beletskaya's catalyst) for C−C coupling are: (a) Bumagin, N. A.; Bumagina, I. G.; Beletskaya, I. P. *Dokl. Akad. Nauk SSSR* **1984**, *274*, 1103; *Dokl. Chem.* **1984**, *274*, 653. (b) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.

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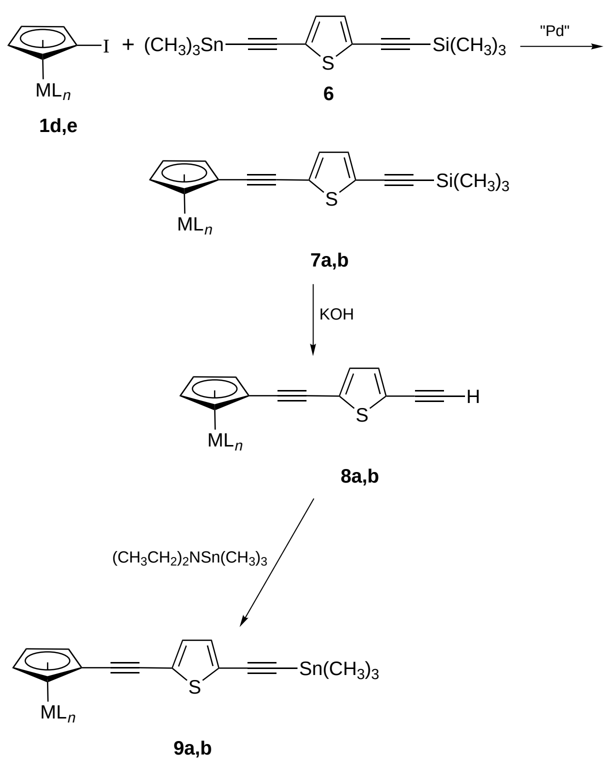
(9) (a) Stille J. K.; Simpson, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 2138. (b) Recently there has been developed a palladium-catalyzed procedure to couple organosilanes and organic electrophiles (Hiyama reaction).[10] However, it occurs under reaction conditions much different from those used here.

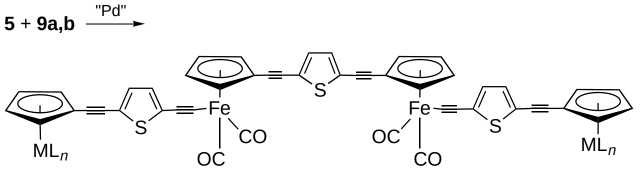
Scheme 2[a]



[a] Legend: (**a**, **d**) $ML_n = W(CO)_3CH_3$; (**b**, **e**) $ML_n = Re(CO)_3$.

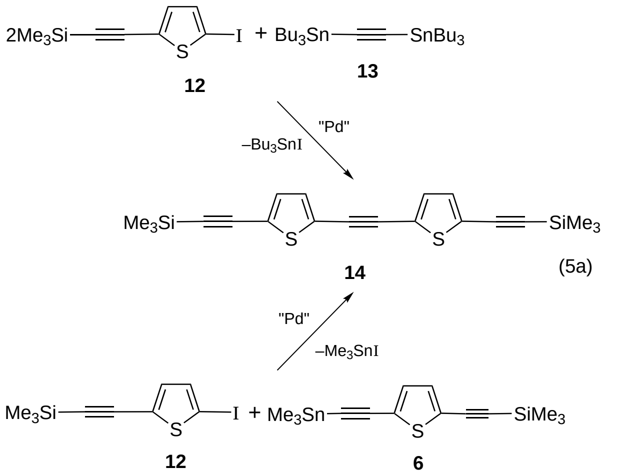
isolated yields, respectively. Removal of the TMS protecting group form **7a,b** was easily accomplished by treatment with a catalytic amount of KOH in methanol,[11] to give free alkynes **8a,b** in 70% and 83% yields, respectively. Final treatment with Et_2NSnMe_3 afforded complexes **9a,b,** which have an activated acetylenic *terminus* ready to be coupled to the bis(iron iodide) complex **5** (eq 3).

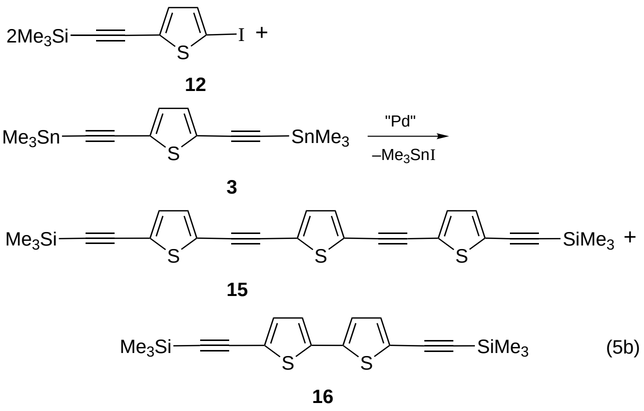
Coupling reactions were carried out under the usual conditions:[4] 5% $(CH_3CN)_2PdCl_2$ as a precatalyst, a slight excess of stannane to promote the in situ reduction of Pd^{II} to the catalytically active Pd^0,[12] DMF solvent, room temperature. Subsequent workup and isolation of products was carried out as follows. The solvent and the Me_3SnI byproduct were removed in vacuo. The residue was purified by column chromatography to afford the tetrametallic complexes **10** and **11** in 21% and 58% yields, respectively (eq 4).



10, $ML_n = W(CO)_3CH_3$
11, $ML_n = Re(CO)_3$

To investigate further the potential of Pd catalysis in the construction of poly(metallaacetylide) tethers, we prepared several types of polyacetylenic spacers. Taking inspiration from the synthetic routes leading to the bis(ethynyl)thiophene derivatives 2,5-bis[(trimethylstannyl)ethynyl]thiophene (**3**) and 2-[(trimethylsilyl)ethynyl]-5-[(trimethylstannyl)ethynyl]thiophene[4d] (**6**), we prepared the poly(ethynylthiophene) **14** by Stille coupling of 2 equiv of 2-iodo-5-(trimethylsilyl)thiophene[4d] (**12**) with 1 equiv of bis(tributylstannyl)acetylene (**13**) (eq 5a). Compound **14** was prepared also by coupling an equivalent amount of **12** and **6**. The first route afforded the coupled product in a nearly quantitative yield, while the second path gave 68% yield. The former route has an additional advantage in that **13** is commercially available, whereas **6** must be prepared in two steps[4d] from **12**. To obtain the higher order oligomer **15**, 2 equiv of 2-iodo-5-(trimethylsilyl)thiophene (**12**) was coupled, under Stille conditions, with 1 equiv of 2,5-bis[(trimethylstannyl)ethynyl]thiophene (**3**) (eq 5b). In this reaction the expected trimer **15**, derived from cross coupling and isolated in 53% yield, was accompanied with a considerable amount (18%) of the dimer **16**, probably formed by homocoupling[12] of 2-iodo-5-(trimethylsilyl)thiophene (**12**). This side product was not observed in the formation of **14** or in our previous work when **12** was coupled with $Bu_3SnC{\equiv}CH$ in the presence of $(CH_3CN)_2PdCl_2$ to form 2-[(trimethylsilyl)ethynyl]-5-(ethynyl)thiophene.[4d]





Compound **16**, as well as **14** and **15**, might be used to widen the range of viable spacers for the construction of poly(metallaacetylide) tethers. Replacement of the TMS protecting groups by the trialkyltin moieties made compounds **14**−**16** reactive in the Pd-catalyzed coupling.

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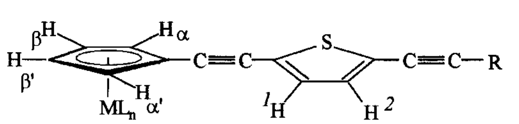
[10] Mateo, C.; Fernandez-Rivas, C.; Echavarren, A.; Cardenas, D. J. *Organometallics* **1997**, *16*, 1997 and references therein.

[11] Neenan, T. X.; Whitesides, G. M. *J. Org. Chem.* **1988**, *53*, 2489.

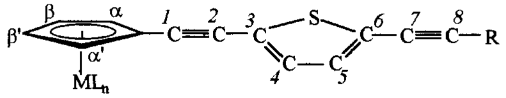
[12] Pugh, C.; Percec, V. *J. Polym. Sci., Part A: Polym. Chem. Ed.* **1990**, *28*, 1101.

Table 1. ^1H and ^{13}C NMR Data (δ, ppm) for Compounds 7a,b−9a,b



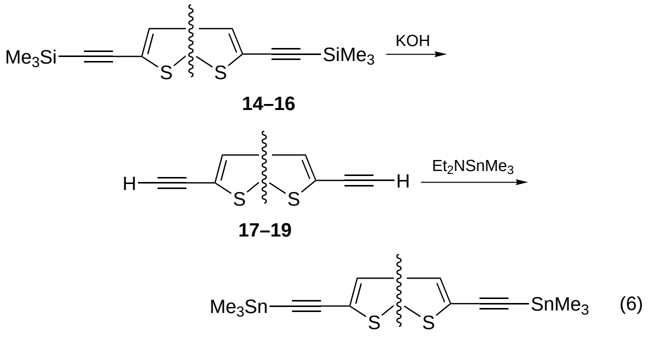
7a); MLn=W(CO)$_3$CH$_3$, R=Si(CH$_3$)$_3$
7b); MLn=Re(CO)$_3$, R=Si(CH$_3$)$_3$
8a); MLn=W(CO)$_3$CH$_3$, R=H
8b); MLn=Re(CO)$_3$, R=H
9a); MLn=W(CO)$_3$CH$_3$, R=Sn(CH$_3$)$_3$
9b); MLn=Re(CO)$_3$, R=Sn(CH$_3$)$_3$

^1H NMR	β–β'	α–α'	*1, 2*		*CH$_3$*	*R*
7a)	5.56, t, J=2.29Hz, 2H	5.30, t, J=2.29Hz, 2H	7.11, s, 2H		0.55, s, 3H	0.22, s, 9H
7b)	5.67, t, J=2.22Hz, 2H	5.30, t, J=2.22Hz, 2H	7.06, d, J=3.85Hz, 1H	7.03, d, J=3.85Hz, 1H		0.22, s, 9H
8a)	5.56, t, J=2.37Hz, 2H	5.31, t, J=2.37Hz, 2H	7.12, d, J=3.85Hz, 1H	7.08, d, J=3.85Hz, 1H	0.55, s, 3H	3.36, s, 1H
8b)	5.67, t, J=2.22Hz, 2H	5.30, t, J=2.22Hz, 2H	7.11, d, J=3.85Hz, 1H	7.06, d, J=3.85Hz, 1H		3.36, s, 1H
9a)	5.56, t, J=2.37Hz, 2H	5.30, t, J=2.37Hz, 2H	7.05, d, J=3.85Hz, 1H	7.02, d, J=3.85Hz, 1H	0.55, s, 3H	0.34, s, 9H 0.44, d, J=1.33Hz } $Sn^{117\text{-}119}$ 0.24, d, J=1.33Hz } satellites
9b)	5.66, t, J=2.37Hz, 2H	5.29, t, J=2.37Hz, 2H	7.02, d, J=3.85Hz, 1H	7.01, d, J=3.85Hz, 1H		0.34, s, 9H 0.44, d, J=1.33Hz } $Sn^{117\text{-}119}$ 0.24, d, J=1.33Hz } satellites



^{13}C NMR	β–β' α–α' *ipso*	*1, 2*	*3, 6*	*4, 5*	*7, 8*	*(CO)$_3$*	*CH$_3$*	*R*
7a)	94.29, 89.03, 92.72	100.64, 96.57	125.33, 122.98	132.54, 132.40	85.15, 83.56	227.83, 214.87	-28.04	-0.28
7b)	87.98, 83.96, 81.85	100.58, 96.55	125.18, 122.98	132.35	84.83, 84.27	192.91		-0.32
8a)	94.25, 89.11, 92.37	85.32, 83.23	123.92, 123.37	132.87, 132.46	82.69, 76.13	227.81, 214.86	-28.12	
8b)	87.87, 83.77, 81.44	84.70, 83.92	123.69, 123.21	132.66, 132.06	82.30, 75.95	192.72		
9a)	94.04, 88.87, 92.58	101.08, 100.03	125.76, 121.94	132.36, 131.58	84.74, 83.50	227.71, 214.75	-28.11	-7.80
9b)	87.75, 83.92, 81.75	100.97, 99.93	125.59, 121.91	132.11, 131.49	84.37, 84.16	192.75		-7.92

This transformation was easily accomplished by first cleaving the TMS groups with a catalytic amount of KOH[11] in a mixture of methanol and THF and then treating the corresponding free alkynes **17**−**19** with Et$_2$NSnMe$_3$[4d] (eq 6).



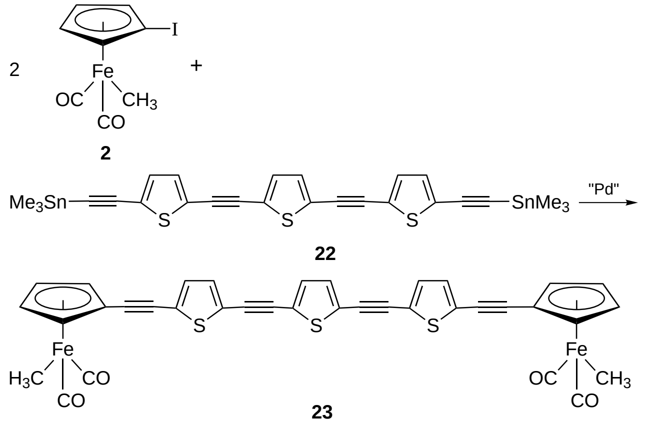
14–16

17–19

(6)

20–22

Compound **22** was then subjected to Stille coupling with the (η^5-iodocyclopentadienyl)iron dicarbonyl methyl complex **2**, forming **23** in 16% yield (eq 7).



2

22

23

(7)

NMR Characterization. Tables 1−3 show the NMR data (^{1}H and ^{13}C) of compounds **7a,b**−**9a,b**, **10** and **11**, and **14**−**23**, respectively. α−α′ and β−β′ assignments for the cyclopentadienyl moieties have been attributed according to literature reports.[14] Thiophene resonances are consistent with those observed for related compounds.[4b−d,15] In complexes **10** and **11** (Table 2) the tungsten and the rhenium pendants as well as the central bis(iron) moiety mostly maintain the same spectroscopic features of the corresponding precursors **7a**−**9a**, **7b**−**9b** (Table 1), and **5**. In complexes **7a**−**9a** and **7b**−**9b** it has been possible to distinctly assign the −C(1)≡C(2)− and −C(7)≡C(8)− carbon resonances. This distinction has been also possible on the basis of the spectroscopic trend observed for the −C≡C− signals of the thiophene compounds listed in Table 3. The progressive change of the R substituent in complexes **7a,b**−**9a,b** as well as in compounds **14**−**22** always produces the same effects on chemical shifts of the −C≡C− moiety carrying the R substituents; then it becomes easily distinguishable from the other acetylene unit, which is less influenced by the substitution. In the proton spectra of the bis(ethynyl)thiophene dimer **17** the acetylenic protons appear as a narrow doublet (J = 0.4 Hz). This splitting is caused by the coupling

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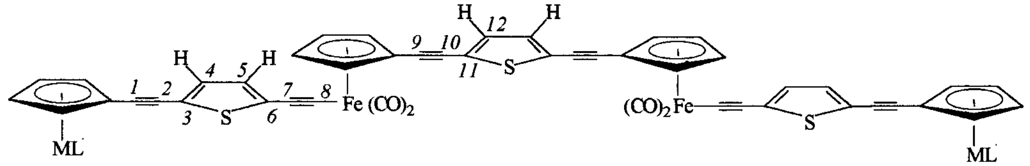
(13) (a) Tsuji, J. *Palladium Reagents and Catalysts*; Wiley: Chichester, England, 1996. (b) Itahara, T. *J. Org. Chem.* **1985**, *50*, 5272.

(14) Koridze, A. A.; Petrovskii, P. V.; Mokhov, A. I.; Lutsenko, A. I. *J. Organomet. Chem.* **1977**, *136*, 57.

(15) Tormos, G. V.; Nugara, P. N.; Lakshmikantham, M. V.; Cava, M. P. *Synth. Met.* **1993**, *53*, 271.

Table 2. ^{1}H and ^{13}C NMR Data (δ, ppm) for Compounds 10 and 11



10) ML_n = $W(CO)_3CH_3$
11) ML_n = $Re(CO)_3$

^{1}H MNR	(η^5-C_5H_4)ML_n β–β' α–α'	ML_n CH_3		4, 5			(η^5-C_5H_4)Fe β–β' α–α'		12
10)	5.26, t, J=2.15 Hz, 2H 5.06, t, J=2.15 Hz, 2H	0.54, s, 3H		6.98, d, J=3.70 Hz, 2H 6.72, d, J=3.85 Hz, 2H			5.54, t, J=2.20 Hz, 2H 5.30, t, J=2.20 Hz, 2H		7.16, s, 2H
11)	5.29, t, J=2.15 Hz, 2H 5.05, t, J=2.15 Hz, 2H			6.95, d, J=3.70 Hz, 2H 6.72, d, J=3.85 Hz, 2H			5.62, t, J=2.20 Hz, 2H 5.26, t, J=2.20 Hz, 2H		7.15, s, 2H
^{13}C MNR	β–β' α–α' ipso	M(CO)$_3$ CH_3	1, 2	3, 4, 5, 6	7, 8	Fe(CO)$_2$	β–β' α–α' ipso	9, 10	11, 12
10)	94.00, 84.44, 94.32	215.15 -27.30 228.21	107.66, 99.70	133.16, 128.40, 130.99, 117.88	87.52, 85.69	210.72	88.41, 84.80, 84.11	83.04, 81.35	124.05, 133.41
11)	87.65, 83.83, 83.66	193.21	107.69, 99.43	132.44, 128.43, 130.99, 117.97	85.90, 85.71	210.74	88.44, 84.82, 84.13	83.20, 82.67	124.11, 133.21

with the thiophene proton adjacent to the acetylenic branch, which appears as a doublet of doublets, while the other thiophenic protons, too far to couple with the acetylenic protons, appear as a simple doublet. This fine splitting is not observed in the other bis(ethynyl)-thiophene oligomers **18** and **19**.

Conclusion

Compounds **10**, **11**, and **23** represent intriguing examples of poly(metallaacetylide) tethers which have been made accessible by combining Stille coupling and Pd-catalyzed metal−carbon bond formation methodologies. The synthetic protocol leading to the thiophene oligomers **14**−**22** may constitute a complementary approach to that of Dixneuf[16] and of Cava[15] for the construction of polyaromatic polyacetylide spacers.

Experimental Section

General Procedures. Elemental analyses were performed by the Servizio Microanalisi of the Area della Ricerca di Roma (CNR, Montelibretti, Italy). IR spectra were recorded on a Nicolet FT 510 instrument in the solvent subtraction mode, using a 0.1 mm CaF_2 cell. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC300P spectrometer at 300 and 75 MHz, respectively. The ^{1}H NMR chemical shifts are reported in ppm downfield vs Me_4Si, assigning the residual ^{1}H 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. GC-MS analyses were performed on a HP5890 GC (OV1 capillary column, 12 m × 0.2 mm) coupled with a HP5970 MSD. Solvents, including those used for NMR and chromatography, and liquids were thoroughly degassed before use. Chromatographic separations were performed with 70−230 mesh silica gel (Merck).

Standard techniques, with Schlenk type equipment for the manipulation of air-sensitive compounds under a blanket of argon, were employed. All solvents were dried (sodium−potassium alloy for tetrahydrofuran (THF), CaH_2 for *N*,*N*-dimethylformamide (DMF), and P_2O_5 for CH_2Cl_2) and argon-saturated prior to use. The following compounds were prepared by known methods: (η^5-C_5H_4I)Fe(CO)$_2$CH$_3$,[6a] (η^5-C_5H_4I)Re(CO)$_3$,[6a] (η^5-C_5H_4I)W(CO)$_3$CH$_3$,[6a] 2-[(trimethylsilyl)ethynyl]-5-[(trimethylstannyl)ethynyl]thiophene,[4d] 2-iodo-5-(trimethylsilyl)-thiophene,[4d] $(CH_3CN)_2PdCl_2$,[17] $(PPh_3)_4Pd$,[18] $(CH_3CH_2)_2NSn(CH_3)_3$.[19] 2,5-Bis[(trimethylstannyl)ethynyl]thiophene (**3**) was quantitatively obtained by treatment of 2,5-bis(ethynyl)-thiophene[11] with 2 equiv of $(CH_3CH_2)_2NSn(CH_3)_3$ as described for a similar compound.[4b] IR (CH_2Cl_2): 2126.2 (m) cm^{-1}.^{1}H NMR (300 MHz, $CDCl_3$): δ 6.97 (s, 2H), 0.43 (d, J = 1.3 Hz, $^{117-119}$Sn satellites), 0.34 (s, 18H), 0.23 (d, J = 1.3 Hz, $^{117-119}$Sn satellites). ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.67, 124.25, 100.65, 99.66, −7.68. Anal. Calcd for $C_{14}H_{20}SSn_2$: C, 36.73; H, 4.40. Found: C, 36.80; H, 4.51.

Preparation of Complex 4, $CH_3(CO)_2Fe(\eta^5\text{-}C_5H_4)C{\equiv}C\text{-}C{=}CHSCH{=}CC{=}C(\eta^5\text{-}C_5H_4)Fe(CO)_2CH_3$. To a solution of 6.90 g (21.7 mmol) of (η^5-C_5H_4I)Fe(CO)$_2$CH$_3$ (**2**) and 5.46 g (11.92 mmol) of 2,5-bis[(trimethylstannyl)ethynyl]thiophene (**3**) in 20 mL of DMF was added 0.15 g (0.6 mmol) of $(CH_3CN)_2PdCl_2$. The mixture was stirred overnight at room temperature; then 50 mL of ether was added and the solution was transferred into a separatory funnel. The ether solution was washed three times with 100 mL portions of water, and the combined aqueous solutions were extracted twice with 50 mL portions of ether. The combined ether extracts were dried over magnesium sulfate and filtered. A 10 g amount of Celite was added to the filtrate and the mixture was evaporated to dryness in vacuo. The residue was placed on a chromatographic column packed with silica and eluted with a mixture of 5% EtOAc in hexanes. Pure product was recovered (4.9 g, 88%) as yellow solid.

IR (CH_2Cl_2): 3056.6 (s), 2011 (vs), 1954.4 (vs) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.08 (s, 2H), 4.95 (t, J = 2.22 Hz, 4H), 4.77 (t, J = 2.22 Hz, 4H), 0.35 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 216.14, 132.30, 124.24, 89.39, 87.39, 83.65, 83.45, 81.83, −18.95. Anal. Calcd for $C_{24}H_{16}O_4Fe_2S$: C, 56.29; H, 3.15. Found: C, 56.49; H, 3.30.

Preparation of Complex 5, $I(CO)_2Fe(\eta^5\text{-}C_5H_4)C{\equiv}C\text{-}C{=}CHSCH{=}CC{=}C(\eta^5\text{-}C_5H_4)Fe(CO)_2I$. $CH_3(CO)_2Fe(\eta^5\text{-}C_5H_4)C{\equiv}CC{=}CHSCH{=}CC{\equiv}C(\eta^5\text{-}C_5H_4)Fe(CO)_2CH_3$ (**4**; 4.85 g, 9.47 mmol) was dissolved in dichloromethane (150 mL), and the solution was cooled to 0 °C. Iodine (5.0 g, 19.70 mmol) dissolved in dichloromethane (150 mL) was added, and the mixture was stirred; after 15 min, the solvent was removed

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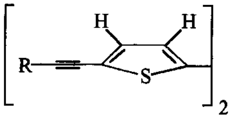
[16] Lavastre, O.; Ollivier, L.; Dixneuf, P. H. *Tetrahedron* **1996**, *52*, 5495.

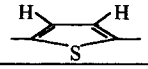
[17] Doyle, J. R.; Slade, P. E.; Jonassen, H. B. *Inorg. Synth.* **1960**, *6*, 216.

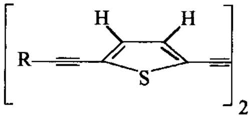
[18] Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.

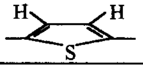
[19] Jones, K.; Lappert, M. F. *J. Chem. Soc.* **1965**, 1944.

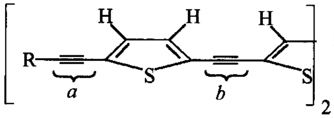
Table 3. ^{1}H and ^{13}C NMR Data (δ, ppm) for Compounds 14−23

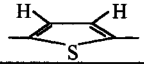
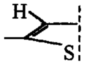


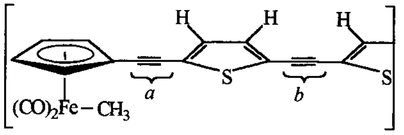
		R		—C≡C—	R
^{1}H NMR	16)	$Si(CH_3)_3$	7.09, d, J=3.84Hz, 2H 6.98, d, J=3.84Hz, 2H		0.22, s, 18H
	17)	H	7.14, dd, J_{ab}=0.4 Hz, J_{bc}=3.77Hz, 2H 6.99, d, J=3.77Hz, 2H		3.39, d, J_{ab}=0.4 Hz, 2H
	20)	$Sn(CH_3)_3$	7.05, d, J=3.77Hz, 2H 6.95, d, J=3.77Hz, 2H		0.34, s, 18H 0.44, d, J=1.33Hz 0.24, d, J=1.33Hz } $Sn^{117-119}$ satellites
^{13}C NMR	16)	$Si(CH_3)_3$	137.92, 133.45, 123.72, 122.45	100.47, 97.14	-0.19
	17)	H	138.03, 133.92, 123.85, 121.37	82.63, 67.93	
	20)	$Sn(CH_3)_3$	137.33, 132.79, 123.48, 122.81	100.81, 100.46	-7.68



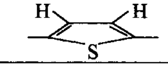
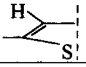
		R		—C≡C—	—C≡	R
^{1}H NMR	14)	$Si(CH_3)_3$	7.08, s, 4H			0.23, s, 18H
	18)	H	7.14, d, J=3.85Hz, 2H 7.10, d, J=3.85Hz, 2H			3.38, s, 2H
	21)	$Sn(CH_3)_3$	7.06, d, J=3.85Hz, 2H 7.03, d, J=3.85Hz, 2H			0.34, s, 18H 0.44, d, J=1.26Hz 0.24, d, J=1.26Hz } $Sn^{117-119}$ satellites
^{13}C NMR	14)	$Si(CH_3)_3$	131.98, 125.66, 123.00	100.91, 86.45	100.39	-7.65
	18)	H	132.98, 132.03, 123.94	82.66, 76.26	86.45	
	21)	$Sn(CH_3)_3$	131.98, 125.66, 123.00	100.91, 100.39	86.45	-7.65



		R			b —C≡C—	a —C≡C—	R
^{1}H NMR	15)	$Si(CH_3)_3$	7.09, s, 4H	7.14, s, 2H			0.23, s, 18H
	19)	H	7.14, d, J=3.85Hz, 2H 7.11, d, J=3.85Hz, 2H	7.15, s, 2H			3.38, s, 2H
	22)	$Sn(CH_3)_3$	7.08, d, J=3.80Hz, 2H 7.04, d, J=3.80Hz, 2H	7.12, s, 2H			0.34, s, 18H 0.45, d, J=1.18Hz 0.25, d, J=1.18Hz } $Sn^{117-119}$ satellites
^{13}C NMR	15)	$Si(CH_3)_3$	132.38, 132.14, 131.94, 125.08, 124.21, 123.40		100.53, 96.54	87.10, 86.37	-0.43
	19)	H	132.98, 132.38, 132.02, 124.32, 123.95		87.06, 86.59	82.74, 76.26	
	22)	$Sn(CH_3)_3$	132.15, 132.03, 131.87, 125.79, 124.29, 122.68		101.06, 100.29	87.37, 86.22	-7.72



23

	(η^5-C_5H_4)Fe							
	α–α'	β–β'	ipso	CH_3			b —C≡C—	a —C≡C—
^{1}H NMR	4.98-4.95, m, 4H 4.80-4.77, m, 4H			0.36, s, 6H	7.13-7.12, m, 4H	7.15, s, 2H		
^{13}C NMR	132.98, 132.98, 132.02			86.45	132.38, 132.14, 131.94, 125.08, 124.21, 123.40		100.53, 96.54	87.10, 86.37

in vacuo. The product was purified by column chromatography on silica using hexanes/EtOAc (2/1) as the eluant to give 3.46 g (50% yield) of **5a** as a dark solid.

IR (CH$_2$Cl$_2$): 2056.2 (s), 2045.3 (sh), 2012.9 (vs) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.19 (s, 2H), 5.26 (t, $J = 2.22$ Hz, 4H), 5.08 (t, $J = 2.22$ Hz, 4H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 212.20, 133.35, 123.98, 87.58, 85.73, 84.46, 83.58, 81.25. Anal. Calcd for C$_{22}$H$_{10}$O$_4$Fe$_2$I$_2$S: C, 35.91; H, 1.37. Found: C, 36.02; H, 1.42.

Preparation of Complexes 7a,b. CH$_3$(CO)$_3$W(η^5-C$_5$H$_4$)-C≡CC=CHSCH≡CC=CSi(CH$_3$)$_3$ (7a). To a solution of 1.4 g (2.95 mmol) of (η^5-C$_5$H$_4$I)W(CO)$_3$CH$_3$ and 1.08 g (2.95 mmol) of 2-[(trimethylsilyl)ethynyl]-5-[(trimethylstannyl)ethynyl]-thiophene (**6**) in 20 mL of THF was added 0.16 g (0.15 mmol) of (PPh$_3$)$_3$Pd. The mixture was stirred at 60 °C for 18 h, then 5 g of Celite was added after cooling, and the mixture was evaporated under reduced pressure to a dry powder. The residue was chromatographed on silica with hexanes/dichloromethane (4/1) to yield 1.34 g (83%) of a brown oil.

IR (CH$_2$Cl$_2$): 2017.5 (vs), 1923.6 (vs) cm^{-1}. Anal. Calcd for C$_{20}$H$_{18}$O$_3$SSiW: C, 43.65; H, 3.30. Found: C, 43.82; H, 3.33.

(CO)$_3$Re(η^5-C$_5$H$_4$)C≡CC=CHSCH=CC≡CSi(CH$_3$)$_3$ (7b). This compound was prepared as described for **7a** from 1.49 g (3.23 mmol) of (η^5-C$_5$H$_4$I)Re(CO)$_3$ (**2e**), 1.30 g (3.55 mmol) of 2-[(trimethylsilyl)ethynyl]-5-[(trimethylstannyl)ethynyl]-thiophene (**6**), and 0.041 g (0.16 mmol) of (CH$_3$CN)$_2$PdCl$_2$. A total of 1.65 g (95%) of product was obtained as a red solid.

IR (CH$_2$Cl$_2$): 2027.2 (vs), 1932.2 (vs) cm^{-1}. Anal. Calcd for C$_{19}$H$_{15}$O$_3$SSiRe: C, 42.44; H, 2.81. Found: C, 42.24; H, 2.75.

Preparation of Complexes 8a,b. CH$_3$(CO)$_3$W(η^5-C$_5$H$_4$)-C≡CC=CHSCH=CC≡CH (8a). To a solution of CH$_3$(CO)$_3$W-(η^5-C$_5$H$_4$)C≡CC=CHSCH=CC≡CSi(CH$_3$)$_3$ (**7a**; 1.13 g, 2.05 mmol) in degassed methanol (100 mL) was added 0.5 mL of a 0.5 M solution of KOH in water (0.014 g, 0.25 mmol). The mixture was stirred at room temperature for 1 h; then the solvent was removed under reduced pressure. The residue was redissolved in a minimum amount of CH$_2$Cl$_2$ and passed through a short (3 × 5 cm) silica column, using the same solvent as eluant. Removal of the solvent under reduced pressure provided 0.69 g (70%) of a yellow liquid.

IR (CH$_2$Cl$_2$): 2017.6 (vs), 1923.1 (vs) cm^{-1}. Anal. Calcd for C$_{17}$H$_{10}$O$_3$SW: C, 42.70; H, 2.11. Found: C, 42.83; H, 2.23.

(CO)$_3$Re(η^5-C$_5$H$_4$)C≡CC=CHSCH=CC≡CH (8b). This compound was prepared as described for **8a** from 0.997 g (1.85 mmol) of (CO)$_3$Re(η^5-C$_5$H$_4$)C≡CC=CHSCH=CC≡CSi(CH$_3$)$_3$ (**7b**) and 0.5 mL of a 0.5 M solution of KOH in water. A total of 0.720 g (83%) of product was obtained as a red solid.

IR (CH$_2$Cl$_2$): 2027.2 (vs), 1933.3 (vs) cm^{-1}. Anal. Calcd for C$_{16}$H$_7$O$_3$SRe: C, 41.28; H, 1.52. Found: C, 41.38; H, 1.71.

Preparation of Complexes 9a,b. CH$_3$(CO)$_3$W(η^5-C$_5$H$_4$)-C≡CC=CHSCH=CC≡CSn(CH$_3$)$_3$ (9a). A mixture of 0.681 g (1.42 mmol) of CH$_3$(CO)$_3$W(η^5-C$_5$H$_4$)C≡CC=CHSCH=CC≡CH (**8a**) and 0.36 g (1.55 mmol) of (CH$_3$CH$_2$)$_2$NSn(CH$_3$)$_3$ was stirred at room temperature for 1 h. After evacuation of the diethylamine byproduct and the tin amide excess, 0.92 g of the product (quantitative conversion) was recovered as a yellow oil.

IR (CH$_2$Cl$_2$): 2017.5 (vs), 1923.2 (vs) cm^{-1}. Anal. Calcd for C$_{20}$H$_{18}$O$_3$SSnW: C, 37.48; H, 2.83. Found: C, 37.34; H, 2.87.

(CO)$_3$Re(η^5-C$_5$H$_4$)C≡CC=CHSCH=CC≡CSn(CH$_3$)$_3$ (9b). This compound was prepared as described for **9a** from 0.720 g (1.54 mmol) of (CO)$_3$Re(η^5-C$_5$H$_4$)C≡CC=CHSCH=CC≡CH (**8b**) and 0.437 g (1.85 mmol) of (CH$_3$CH$_2$)$_2$NSn(CH$_3$)$_3$. Complex **9b** was quantitatively obtained (0.972 g) as a red solid.

IR (CH$_2$Cl$_2$): 2027.2 (vs), 1933.2 (vs) cm^{-1}. Anal. Calcd for C$_{19}$H$_{15}$O$_3$SSnRe: C, 36.32; H, 2.41. Found: C, 36.26; H, 2.31.

Preparation of Complexes 10 and 11. CH$_3$(CO)$_3$W(η^5-C$_5$H$_4$)C≡CC=CHSCH=CC≡CFe(CO)$_2$(η^5-C$_5$H$_4$)C≡C-C=CHSCH=CC≡C(η^5-C$_5$H$_4$)(CO)$_2$FeC≡CC=CHSCH=C-C≡C(η^5-C$_5$H$_4$)W(CO)$_3$CH$_3$ (10). To a solution of 0.35 g (0.475 mmol) of I(CO)$_2$Fe(η^5-C$_5$H$_4$)C≡CC=CHSCH=CC≡C(η^5-C$_5$H$_4$)-Fe(CO)$_2$I (**5a**) and 0.640 g (0.998 mmol) of CH$_3$(CO)$_3$W(η^5-C$_5$H$_4$)C≡CC=CHSCH=CC≡CSn(CH$_3$)$_3$ (**9a**) in 20 mL of DMF was added 0.012 g (0.047 mmol) of (CH$_3$CN)$_2$PdCl$_2$. The reaction mixture was stirred overnight at room temperature, then 5 g of Celite was added. All volatiles (solvent and (CH$_3$)$_3$-SnI) were then vacuum-transferred at 0.01 mmHg, and the residue was chromatographed on silica gel with hexanes/CH$_2$-Cl$_2$ (9/1) to yield 400 mg (58%) of a dark red solid.

IR (CH$_2$Cl$_2$): 2096.9 (m), 2047.0 (vs), 2016.2 (vs), 2006.7 (sh), 1922.1 (vs) cm^{-1}. Anal. Calcd for C$_{56}$H$_{28}$O$_{10}$Fe$_2$S$_3$W$_2$: C, 46.83; H, 1.96. Found: C, 46.73; H, 2.03.

(CO)$_3$Re(η^5-C$_5$H$_4$)C≡CC=CHSCH=CC≡CFe(CO)$_2$(η^5-C$_5$H$_4$)C≡CC=CHSCH=CC≡C(η^5-C$_5$H$_4$)(CO)$_2$FeC≡C-C=CHSCH=CC≡C(η^5-C$_5$H$_4$)Re(CO)$_3$ (11). This compound was prepared as described for **10** from 0.89 g (1.416 mmol) of (CO)$_3$Re(η^5-C$_5$H$_4$)C≡CC=CHSCH=CC≡CSn(CH$_3$)$_3$ (**9b**), 0.47 g (0.644 mmol) of I(CO)$_2$Fe(η^5-C$_5$H$_4$)C≡CC=CHSCH=CC≡C-(η^5-C$_5$H$_4$)Fe(CO)$_2$I (**5a**), and 0.016 g (0.064 mmol) of (CH$_3$-CN)$_2$PdCl$_2$. A total of 0.21 g (23%) of product was obtained as a dark red solid.

IR (CH$_2$Cl$_2$): 2097.4 (w), 2047.5 (m), 2026.4 (vs), 2005.7 (m), 1932.4 (vs) cm^{-1}. Anal. Calcd for C$_{54}$H$_{22}$O$_{10}$Fe$_2$Re$_2$S$_3$: C, 45.97; H, 1.57. Found: C, 45.77; H, 1.53.

Preparation of 14 from Me$_3$SiC≡CC=CHSCH=CI and Bu$_3$SnC≡CSnBu$_3$. To a solution of 0.943 g (3.079 mmol) of 2-iodo-5-(trimethylsilyl)thiophene (**12**) and 1.023 g (1.693 mmol) of bis(tributylstannyl)acetylene (**13**) in 15 mL of DMF was added 0.035 g (0.135 mmol) of (CH$_3$CN)PdCl$_2$. After it was stirred for 3 h at room temperature, the mixture was transferred to a separatory funnel with the aid of 50 mL of CH$_2$Cl$_2$ and washed with water (3 × 50 mL). The aqueous phase was back-extracted with CH$_2$Cl$_2$ (2 × 50 mL), and the combined dichloromethane extracts were washed with water (2 × 50 mL) and dried over sodium sulfate. Following filtration, Celite (5 g) was added to the filtrate and the solvent evaporated. The coated mixture was purified by column chromatography by using hexanes/THF (9:1). Removal of the solvent provided 1.13 g (96%) of pure product as a yellow solid.

IR (CH$_2$Cl$_2$): 2971.1 (w), 2980.7 (w), 2890.1 (w), 2144.0 (m) 1267.3 (s) 1257.7 (s) cm^{-1}. MS: *m/z* 382 (M$^+$), 367 (M$^+$ − CH$_3$). Anal. Calcd for C$_{20}$H$_{22}$S$_2$Si$_2$: C, 62.77; H, 5.79. Found: C, 62.70; H, 5.76.

Preparation of 14 from Me$_3$SiC≡CC=CHSCH=C-C≡CSnMe$_3$ and Me$_3$SiC≡CC=CHSCH=CI. To a solution of 0.31 g (1.012 mmol) of 2-iodo-5-(trimethylsilyl)thiophene (**12**) and 0.409 g (1.113 mmol) of 2-[(trimethylsilyl)ethynyl]-5-[(trimethylstannyl)ethynyl]thiophene (**6**) in 15 mL of DMF was added 0.013 g (0.05 mmol) of (CH$_3$CN)PdCl$_2$. Following overnight stirring at room temperature, the workup and isolation of product were carried out as described above, to yield 0.26 g (68%) of the product as a yellow solid.

Preparation of Me$_3$SiC≡CC=CHSCH=CC≡CC=CHSCH=CC≡CC=CHSCH=CC≡CSiMe$_3$ (15) and Me$_3$SiC≡CC=CHSCH=CC=CHSCH=CC≡CSiMe$_3$ (16). To a solution of 1.172 g (2.56 mmol) of 2,5-bis[(trimethylstannyl)ethynyl]thiophene (**3**) and 1.73 g (5.64 mmol) of 2-iodo-5-(trimethylsilyl)thiophene (**12**) in 15 mL of DMF was added 0.073 g (0.28 mmol) of (CH$_3$CN)PdCl$_2$. Following overnight stirring at room temperature, the mixture was transferred to a separatory funnel with the aid of 50 mL of CH$_2$Cl$_2$ and washed with water (3 × 50 mL). The aqueous phase was back-extracted with CH$_2$Cl$_2$ (2 × 50 mL), and the combined dichloromethane extracts were washed with water (2 × 50 mL) and dried over sodium sulfate. Following filtration, Celite (5 g) was added to the filtrate and the solvent evaporated. The residue was then applied to a silica gel column packed with hexanes/CH$_2$Cl$_2$ (95:5). Elution with a mixture of hexanes and CH$_2$Cl$_2$ (95:5) first removed Me$_3$SiC≡CC=CHSCH=CC=CHSCH=CC≡CSiMe$_3$ (**16**; 0.364 g, 18%) followed by Me$_3$SiC≡CC=CHSCH=CC≡CC=CHSCH=CC≡CC=CHSCH=CC≡CSiMe$_3$ (**15**; 1.46 g, 53%).

Characterization of 15. IR (CH$_2$Cl$_2$): 2961.1 (w), 2928.5 (w), 2856.5 (w), 2143.9 (m), 1267.6 (s), 1262.5 (s) cm^{-1}. Anal. Calcd for C$_{26}$H$_{24}$S$_3$Si$_2$: C, 63.88; H, 4.95. Found: C, 64.02; H, 5.06.

Characterization of 16. IR (CH$_2$Cl$_2$): 2962.9 (w), 2929.3 (w), 2855.5 (w), 2142.8 (m), 1267.8 (s), 1262.9 (s) cm^{-1}. MS: *m/z* 358 (M$^+$), 343 (M$^+$ − CH$_3$). Anal. Calcd for C$_{18}$H$_{22}$S$_2$Si$_2$: C, 60.28; H, 6.18. Found: C, 60.04; H, 6.27.

Preparation of Compounds 17−19. HC≡CC=CHSCH=CC=CHSCH=CC≡CH (17). To a solution of Me$_3$SiC≡CC=CHSCH=CC=CHSCH=CC≡CSiMe$_3$ (**16**; 0.34 g, 0.948 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 until GC analysis indicated that the reaction was complete. The reaction mixture was diluted with water (50 mL) and extracted with pentane (3 × 30 mL). The combined organic layers were dried over sodium sulfate, and following filtration, the solvent was removed at reduced pressure at room temperature. The residue was taken up in the minimum amount of hexanes and chromatographed on silica gel using hexanes as the eluting solvent. Removal of the solvent yielded 0.16 g (82%) of product as a pale yellow oil that darkened upon standing.

IR (CH$_2$Cl$_2$): 3301.2 (w), 2103.1 (w), 1260.6 (s), 1254.2 (s) cm^{-1}. MS: *m/z* 214 (M$^+$).

This compound was used immediately after its preparation.

HC≡CC=CHSCH=CC≡CC=CHSCH=CC≡CH (18). To a solution of Me$_3$SiC≡CC=CHSCH=CC≡CC=CHSCH=CC≡CSiMe$_3$ (**14**; 0.22 g, 0.575 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 the reaction mixture was diluted with water (50 mL) and extracted with pentane (3 × 30 mL). The combined organic layers were dried over sodium sulfate, and following filtration, the solvent was removed at reduced pressure at room temperature. The residue was taken up in the minimum amount of hexanes and chromatographed on silica gel using hexanes as the eluting solvent. Removal of the solvent yielded 0.11 g (82%) of product as a pale yellow oil that darkened upon standing.

IR (CH$_2$Cl$_2$): 3303.3 (w), 3056.4 (w), 2103.2 (w), 1269.2 (s), 1259.2 (s) cm^{-1}.

This compound was used immediately after its preparation.

HC≡CC=CHSCH=CC≡CC=CHSCH=CC≡CC=CHSCH=CC≡CH (19). This compound was prepared by treating 0.72 g (1.47 mmol) of Me$_3$SiC≡CC=CHSCH=CC≡CC=CHSCH=CC≡CC=CHSCH=CC≡CSiMe$_3$ (**15**) in a mixture (30 mL) of THF and methanol (1:1), with 0.1 mL of a 0.5 M solution (0.05 mmol) of KOH in water as described for **18**. The product was isolated by column chromatography on silica gel using a mixture of hexanes and THF (9:1) as the eluting solvent. Removal of the solvent yielded 0.28 g (56%) of the product as a yellow oil that darkened upon standing.

IR (CH$_2$Cl$_2$): 3054.7 (w), 2963.0 (w), 2927.5 (w), 2855.8 (w), 1267.4 (s), 1263.5 (s) cm^{-1}.

This compound was used immediately after its preparation.

Preparation of Compounds 20−22. Me$_3$SnC≡CC=CHSCH=CC=CHSCH=CC≡CSnMe$_3$ (20). A mixture of 0.11 g (0.51 mmol) of neat HC≡CC=CHSCH=CC=CHSCH=CC≡CH (**17**) and 0.13 g (0.565 mmol) of Et$_2$NSnMe$_3$ was stirred at room temperature for 20 min. After removal under vacuum of the diethylamine byproduct and the tin amide excess, pure product was quantitatively recovered as a tan solid.

IR (CH$_2$Cl$_2$): 3056.0 (w), 2121.1 (w), 1270.2 (s), 1264.2 (s) cm^{-1}. Anal. Calcd for C$_{18}$H$_{22}$S$_2$Sn$_2$: C, 40.05; H, 4.11. Found: C, 40.25; H, 4.18.

Me$_3$SnC≡CC=CHSCH=CC≡CC=CHSCH=CC≡CSnMe$_3$ (21). This product was formed by reaction of 0.34 g (1.43 mmol) of neat HC≡CC=CHSCH=CC≡CC=CHSCH=CC≡CH (**18**) and 0.40 g (1.70 mmol) of Et$_2$NSnMe$_3$ as described for **20**. Removal under vacuum of the diethylamine byproduct and the tin amide excess yielded a quantitative amount of pure product as a tan solid.

IR (CH$_2$Cl$_2$): 3054.8 (w), 2120.7 (w), 1269.2 (s), 1260.5 (s) cm^{-1}. Anal. Calcd for C$_{20}$H$_{22}$S$_2$Sn$_2$: C, 42.60; H, 3.93. Found: C, 42.72; H, 3.83.

Me$_3$SnC≡CC=CHSCH=CC≡CC=CHSCH=CC≡CC=CHSCH=CC≡CSnMe$_3$ (22). This product was formed by reaction of 0.28 g (0.82 mmol) of HC≡CC=CHSCH=CC≡CC=CHSCH=CC≡CC=CHSCH=CC≡CH (**19**) and 0.23 g (0.98 mmol) of Et$_2$NSnMe$_3$ as described for **20**. Removal under vacuum of the diethylamine byproduct and the tin amide excess yielded a quantitative amount of pure product as a tan solid.

IR (CH$_2$Cl$_2$): 3057.3 (w), 2120.3 (w), 1264.1 (s) 1258.5 (s) cm^{-1}. Anal. Calcd for C$_{26}$H$_{24}$S$_3$Sn$_2$: C, 46.61; H, 3.61. Found: C, 46.66; H, 3.70.

Preparation of CH$_3$(CO)$_2$Fe(η^5-C$_5$H$_4$)C≡CC=CHSCH=CC≡CC=CHSCH=CC≡CC=CHSCH=CC≡C(η^5-C$_5$H$_4$)Fe(CO)$_2$CH$_3$ (23). This compound was prepared from 0.52 g (1.64 mmol) of (η^5-C$_5$H$_4$I)Fe(CO)$_2$CH$_3$ (**2a**), 0.55 g (0.82 mmol) of Me$_3$SnC≡CC=CHSCH=CC≡CC=CHSCH=CC≡CC=CHSCH=CC≡CSnMe$_3$ (**22**) and 0.007 g (0.03 mmol) of (CH$_3$CN)$_2$PdCl$_2$ in DMF (20 mL) using the procedure described for

4a. The product was isolated by column chromatography on silica gel using a mixture of hexanes and dichloromethane (1:1) as the eluting solvent. Removal of the solvent yielded 0.95 g (16%) of product as a dark solid.

IR (CH_2Cl_2): 2011.1, 1954.5 cm^{-1}. Anal. Calcd for $C_{36}H_{20}O_4Fe_2S_3$: C, 42.60; H, 3.93. Found: C, 42.72; H, 3.83.

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