Formation of a Molybdenum−Iron Heterobimetallic Bis(acetylide) Derivative of 2,5-Diethynylthiophene *via* Palladium-Catalyzed Metal−Carbon Coupling

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Summary: By use of the palladium-catalyzed metal−carbon bond formation reaction, the molybdenum cyclopentadienyl and iron indenyl iodo derivatives (η^5-C_5H_5)-Mo(CO)$_3$I and (η^5-C_9H_7)Fe(CO)$_2$I have been linked in a σ fashion to the ethynyl edges of 2,5-diethynylthiophene to form the heterobimetallic complex (η^5-C_5H_5)(CO)$_3$-MoC≡C(Thiop)C≡CFe(CO)$_2$(η^5-C_9H_7) (Thiop = 2,5-substituted thiophene).

Our recent disclosure of Pd-catalyzed metal−carbon bond formation as a tool to prepare σ-metallaacetylides has both allowed an alternative and convenient access to an important class of compounds and revealed unexpected and fascinating new properties of palladium catalysts.[1] Figure 1 summarizes the variety of mono and bis transition metal σ-acetylides we were able to prepare by the use of this simple and efficient novel methodology.

Innovators in materials science are currently devoting much attention to highly ethynylated organometallic compounds for use in the fields of electronics, optics, and ceramics.[2] This interest is due to the unique chemical and physical properties that may arise from *facile* electron transfer between transition metals throughout the π-unsaturated carbon chain.[3] We were thus interested in further expanding the synthetic possibility of this novel procedure, since complexes such as those reported in Figure 1 may serve as models and/or prototypes for organometallic polyyne polymers. For this study the preparation of heterobimetallic complexes was an attractive target, since the interplay of two different metal groups may allow a fine tuning of properties of these materials.[4]

We pursued our study by aiming at the stepwise introduction of two acetylenic branches and transition-metal units on the thiophene core, as summarized in Scheme 1.[5]

2-[(Trimethylsilyl)ethynyl]thiophene[6] (**5**) was prepared in 74% yield from 2-bromothiophene and (tri-

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(5) Experimental procedures and characterization of new compounds are as follows. **3**: IR (neat) ν/cm^{-1} 2960.3, 2146.0; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.06 (1H, d, J = 3.8 Hz), 6.85 (1H, d, J = 3.8 Hz), 0.22 (9H, s); ^{13}C NMR (71 MHz, $CDCl_3$) δ 136.72, 133.72, 129.32, 100.87, 96.15, 74.86, −0.24; EI MS m/z 306 (M^+), 291 ($M^+ - CH_3$). **4**: IR (neat) ν/cm^{-1} 3304.8, 2960.3, 2147.1, 2103.7; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (1H, d, J = 3.8 Hz), 7.04 (1H, d, J = 3.8 Hz), 3.32 (1H, s), 0.22 (9H, s); ^{13}C NMR (71 MHz, $CDCl_3$) δ 132.69, 132.15, 124.88, 123.18, 100.07, 96.65, 82.01, 76.41, −0.25; EI MS m/z 204 (M^+), 189 ($M^+ - CH_3$). **5**: IR (CH_2Cl_2) ν/cm^{-1} 2144.7, 2123.0; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.01 (1H, d, J = 3.8 Hz), 6.98 (1H, d, J = 3.8 Hz), 0.34 (9H, s), 0.22 (9H, s); ^{13}C NMR (71 MHz, $CDCl_3$) δ 132.26, 131.67, 125.05, 123.66, 100.49, 100.12, 99.46, 97.03, −0.22, −7.68. Anal. Calcd for $C_{14}H_{20}SSiSn$: C, 45.80; H, 5.49. Found: C, 45.99; H, 5.56. **6**: A solution of $(CH_3CN)_2PdCl_2$ (0.09 g, 0.36 mmol) in DMF (5 mL) was added to a mixture of (η^5-C_5H_5)Mo(CO)$_3$I (2.73 g, 7.33 mmol) and **5** (3.24 g, 8.82 mmol) dissolved in dry degassed DMF (30 mL). After 3 h the reaction mixture was transferred to a separatory funnel, diluted with dichloromethane, and washed with water. The organic extract was dried over magnesium sulfate, filtered, and evaporated to dryness. Chromatographic separation on silica gel using a mixture of hexane/EtOAc (3/1) provided 3.06 g (93%) of product as a red solid. IR (CH_2Cl_2): ν/cm^{-1} 2045.5, 1968.6. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.97 (1H, d, J = 3.8 Hz), 6.72 (1H, d, J = 3.8 Hz), 5.54 (5H, s), 0.20 (9H, s). ^{13}C NMR (71 MHz, $CDCl_3$): δ 237.82, 222.08, 132.31, 129.09, 128.40, 120.81, 120.53, 98.23, 98.15, 97.84, 93.00, −0.10. Anal. Calcd for $C_{19}H_{16}MoO_3SSi$: C, 50.89; H, 3.6. Found: C, 51.02; H, 3.9. **7**: Compound **6** (0.79 g, 1.8 mmol) in degassed CH_3CN (30 mL) was cooled to −20 °C, and an equivalent amount of $Bu_4NF{\cdot}3H_2O$ was added. After 5 min, H_2O (100 mL) was added and the mixture extracted with Et_2O (3 × 40 mL). The ethereal extracts were back-extracted with water, dried over $MgSO_4$, and filtered through a glass frit covered with a pad of silica gel. Evaporation under high vacuum left the product as a yellow glassy solid (0.52 g, 78%). IR (CH_2Cl_2): ν/cm^{-1} 2087.7, 2045.3, 1968.0. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.01 (1H, d, J = 3.7 Hz), 6.73 (1H, d, J = 3.7 Hz), 3.24 (1H, s). ^{13}C NMR (71 MHz, $CDCl_3$): δ 237.71, 222.12, 132.69, 129.37, 128.28, 120.27, 119.46, 98.67, 92.99 80.67, 80.54. **8**: Compound **7** (0.44 g, 1.2 mmol) suspended in Et_2O (10 mL) was completely converted into **8** by treatment with Et_2NSnMe_3 (0.42g, 1.8mmol) in an ultrasound bath for 15 min. Removal of volatiles in vacuo left the product as a red-brown powder. IR (CH_2Cl_2): ν/cm^{-1} 2144.7, 2123.0. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.93 (1H, d, J = 3.8 Hz), 6.71 (1H, d, J = 3.8 Hz), 5.54 (5H, s), 0.31 (9H, s). ^{13}C NMR (71 MHz, $CDCl_3$): δ 237.93, 222.10, 132.69, 131.71, 128.35, 121.41, 120.63, 101.45, 98.08, 97.42, 92.99, −7.60. **9**: A solution of $(CH_3CN)_2PdCl_2$ (0.013 g, 0.05 mmol) in DMF (2 mL) was added to a mixture of (η^5-C_9H_7)Fe(CO)$_2$I (0.35 g, 0.98 mmol) and **8** (0.63 g, 1.18 mmol) dissolved in dry degassed DMF (50 mL). After 2 h the solvent was removed by vacuum transfer and the residue chromatographed on silica gel using a mixture of hexane/EtOAc (3/1). Complex **9** was recovered as a red-brown solid (0.25 g, 42%). IR (CH_2Cl_2): ν/cm^{-1} 2091.6, 2043.1, 1993.8, 1967.4. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49 (2H, m), 7.27 (2H, m), 6.63 (1H, d, J = 3.7 Hz), 6.55 (1H, d, J = 3.7 Hz), 5.54 (2H, d, J = 2.8 Hz), 5.53 (5H, s), 5.28 (1H, t, J = 2.8 Hz); ^{13}C NMR (71 MHz, $CDCl_3$): δ 238.73, 222.11, 212.21, 128.99, 128.25, 127.55, 125.29, 125.07, 124.81, 108.67, 103.66, 93.71, 93.02, 72.77. Anal. Calcd for $C_{27}H_{14}FeMoO_5S$: C, 53.85; H, 2.34. Found: C, 54.02; H, 2.42.

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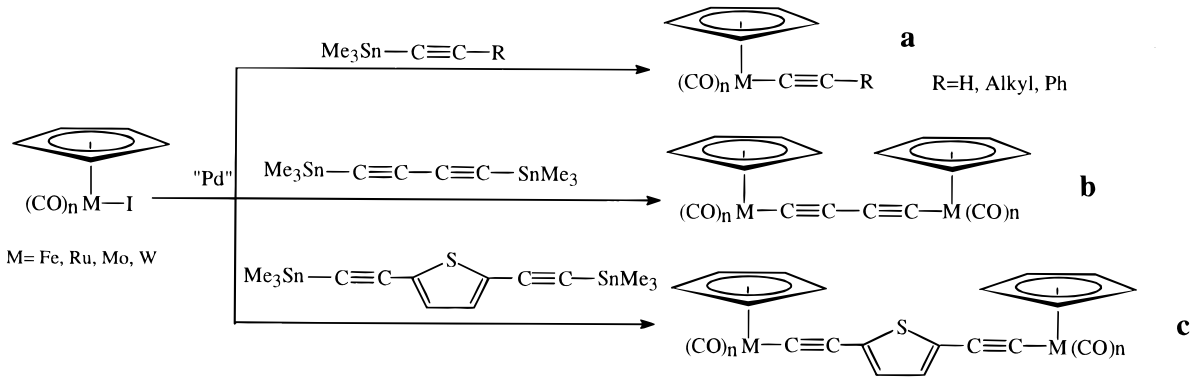
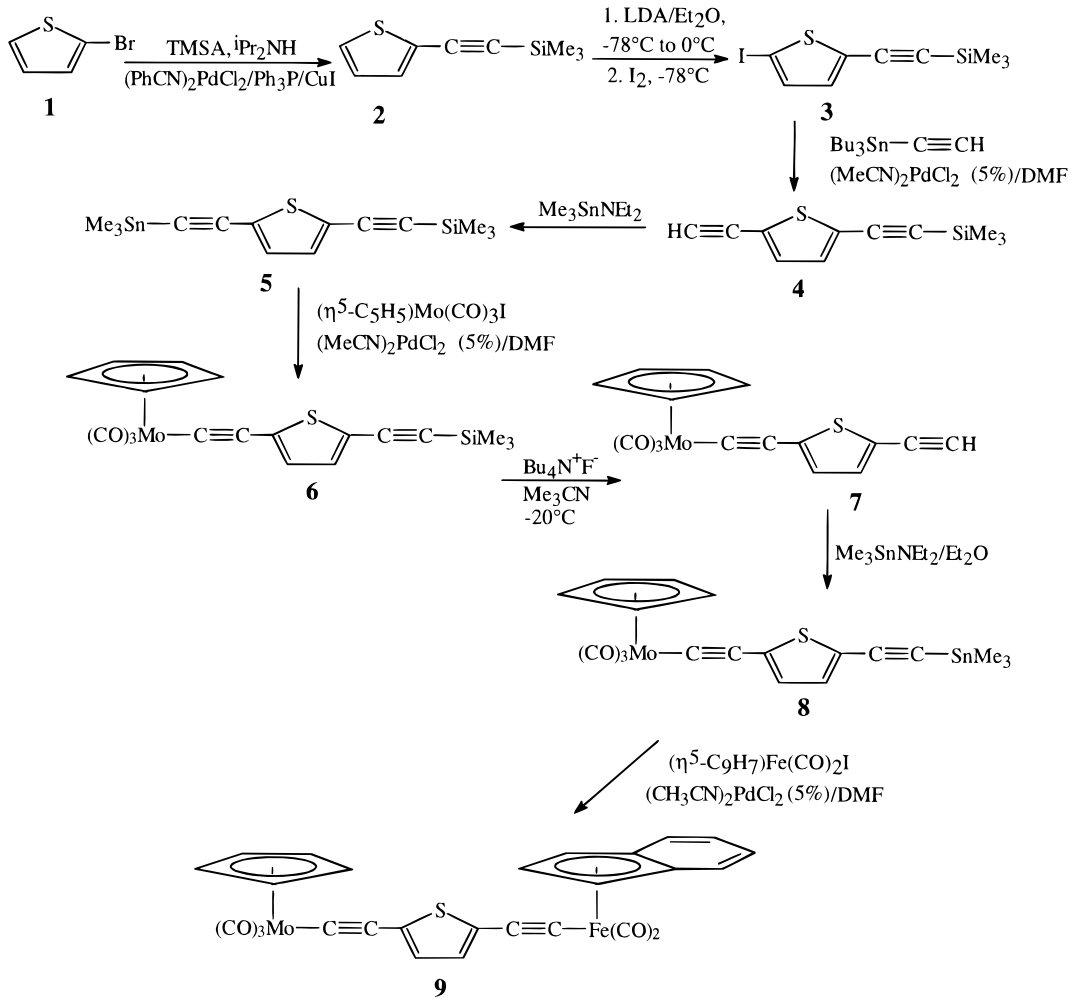


Figure 1.

Scheme 1



methylsilyl)acetylene under the same Pd/Cu catalytic conditions described to prepare 2,5-bis[(trimethylsilyl)-ethynyl]thiophene.[7]

By applying the procedure described by Tour on similar thiophene derivatives,[8] treatment of **2** with LDA and I_2 afforded 2-iodo-5-[(trimethylsilyl)ethynyl]thiophene (**3**) in 92% yield. The Stille coupling[9] performed between compound **3** and tributyltin acetylide in the presence of a catalytic amount (5%) of bis(acetonitrile)-palladium dichloride ($(CH_3CN)_2PdCl_2$) led to the formation of 2-[(trimethylsilyl)ethynyl]-5-ethynylthiophene (**4**).[10] The progress of the reaction was monitored by GC−MS, and formation of the product was complete in 4 h. However, the standard KF treatment[9] usually performed to convert the Bu_3SnI byproduct into the insoluble Bu_3SnF was not suitable in the presence of the labile TMS protecting group. Isolation of pure

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(10) We initially dedicated much effort to the direct formation of **4** by removing a single TMS protecting group from the easily available 2,5-bis[(trimethylsilyl)ethynyl]thiophene.[7] However, despite careful choice of the reaction conditions to limit exposure of this compound to the cleaving effect of the alkaline solution,[7] formation of **4** resulted difficult and unreliable. Our best result was the formation of 43% of 2-[(trimethylsilyl)ethynyl]-5-ethynylthiophene (**4**) that required a careful fractional distillation for separation from fully deprotected 2,5-diethynylthiophene (17%) and unreacted starting material (30%).

product was then performed by column chromatography; however, this had a detrimental effect on the isolated yield (43%).[11] Reaction of **4** with the tin amide[12] Et_2NSnMe_3 produced compound **5**, bearing a single trimethyltin-functionalized acetylenic termination. This reaction was carried out in the absence of solvent and was particularly neat and clean. After addition of compound **4** to a slight excess of the aminostannane, the mixture solidified in 1 h, indicating complete transformation. The excess reactant and the diethylamine byproduct were removed in vacuo, and compound **5** was quantitatively recovered. Compound **5**, bearing a TMS-protected acetylene and a trimethyltin-activated acetylenic moiety, smoothly underwent palladium-catalyzed coupling with $(\eta^5\text{-}C_5H_5)Mo(CO)_3I$ in DMF to form complex **6**. Due to the presence of the trimethylsilyl protecting group, complex **6** showed overwhelming stability, and after workup and chromatographic separation, the product was recovered in 93% yield. In the subsequent step, removal of the trimethylsilyl group to form the free alkyne **7** was a matter of long trial and error. **6** was surprisingly inert toward treatment with alkali,[7] and the use of $Bu_4N^+F^-$ gave a synthetically useful yield (78%) only in CH_3CN at −20 °C. Product **7** is a very sensitive and unstable material, which must be immediately used after its formation. Fortunately, the workup of the reaction mixture afforded a sufficiently pure material to be directly used in the subsequent step. The crude yellow complex **7** remained insoluble upon treatment with an excess of Et_2NSnMe_3, but addition of Et_2O and immersion in an ultrasound bath lead to the formation of a deep red slurry mixture, from which complex **8** was quantitatively isolated after removal of solvent and exposure to high vacuum. Under the same reaction conditions previously used to attach the first metal unit to the trimethyltin acetylide moiety, **8** was coupled with the iron iodide complex $(\eta^5\text{-}C_9H_7)Fe(CO)_2I$ in the presence of a catalytic amount of $(CH_3CN)_2PdCl_2$. After 3 h, a sample of the reaction mixture stripped of solvent and redissolved in $CDCl_3$ showed, by ^1H NMR, that the reagents were completely converted into the product. However, complex **9** proved to be quite unstable and sensitive. Workup and chromatographic separation caused a severe loss of material, the product being isolated in 42% yield.

In conclusion, Scheme 1 summarizes the synthetic cycle forming heterobimetallic complexes and shows three different uses of palladium catalysis: the ethynylation[13] reaction to form **2**, the Stille[14] reaction to form **4**, and the formation of **6** and **9** by the most recently developed procedure, *palladium-catalyzed metal−carbon bond formation*, which in our opinion represents a new and useful tool to access organometallic structures. We are currently devoting much effort to the optimization of reaction procedures and conditions to form and isolate complexes such as **9**.

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(11) The difficulties of eliminating the Bu_3SnI byproduct could be circumvented by using $Me_3SnC{\equiv}CH$ as a coupling partner, since the water-soluble Me_3SnI byproduct would be eliminated during the workup. However, we preferred to maintain this procedure since preparation of $Me_3SnC{\equiv}CH$ requires a troublesome procedure, while $Bu_3SnC{\equiv}CH$ is available from Aldrich and **3** is accessible on a multigram scale.

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