A New Way to both Oligothiophene-Spaced Bimetallic Complexes and Functionalized Oligothiophenes

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Summary: Mono- and binuclear oligothiophene rhodium complexes are obtained by single and double C−S bond cleavage of 2,2′:5′,2″:5″,2‴-quaterthiophene, respectively. S-Methylation of the C−S insertion products, followed by carbonylation of the resulting thioether complexes give the functionalized oligothiophenes 5-[1-(methylthio)-buta-1,3-diene]-2,2′:5′,2″-terthiophene and 5,5′-bis[1-(methylthio)-buta-1,3-diene]-2,2′-bithiophene. The rhodium metal is recovered as a bis(carbonyl) complex.

Oligothiophenes are attractive materials because of their potential applications in the field of electronic and optoelectronic devices.[2,3] Incorporation of transition metals with their large variety of ligand environments and oxidation states is expected to increase the molecular hyperpolarizability and to enhance the already appealing nonlinear optical properties of oligothiophenes.[2c]

The general synthetic methodology for oligothiophene metal complexes has so far involved the preliminary functionalization of the oligothiophene to allow for the appropriate ligating groups to be bonded to the terminal rings.[4]

In this work, we show that this synthetic procedure can efficiently be reversed by exploiting the capability of electron-rich metal fragments to cleave C−S bonds from thiophenes in regioselective manner.[5,6] The approach described here not only allows one-pot access to new structural motifs in which oligothiophenes may act as spacers between metal centers but also provides access to virtually nonexistent oligothiophenes bearing butadienyl functional groups.

The 16-electron fragment [(triphos)RhH], generated *in situ* by thermolysis of the trihydride $[(\text{triphos})\text{RhH}_3]$ (**1**) in refluxing THF,[5a,b] reacts with 2,2′:5′,2″:5″,2‴-quaterthiophene (QT) to give the C−S insertion product $(\text{triphos})\text{Rh}(\eta^3\text{-SC(5-TTyl)=CHCH=CH}_2)$ (TTyl = 2,2′:5′,2″-terthienyl) (**2**) (Scheme 1) [triphos = $\text{MeC(CH}_2\text{PPh}_2)_3$].[7] C−S insertion occurs exclusively into the C_5−S bond of QT, consistent with a determinant steric control.[5a] The sulfur atom in the 5-(TTyl)butadienethiolate ligand is a nucleophilic center, susceptible to attack by MeI.[5,8] As a result, the thioether derivative $[(\text{triphos})\text{Rh}(\eta^3\text{-MeSC(5-TTyl)=CHCH=CH}_2)]\text{BPh}_4$ (**3**) is quantitatively obtained by treatment of **2** in CH_2Cl_2 with MeI followed by metathetical reaction with $NaBPh_4$.[9] The NMR characteristics of **2** and **3** are quite comparable to those of several other butadienethiolate and *S*-methylthiobutadienerhodium complexes,[5a,b,8] respectively. Thus, **2** and **3** are analogously assigned an octahedral structure where the metal center is coordinated by the three phosphorus atoms of a *fac* triphos and by butadienethiolate or methyl butadienyl sulfide ligands which use the sulfur atom and the distal olefinic end to bind the metal. In line with previous reports,[5a,b,8] the $Rh-C_2-C_3$ ring in both compounds exhibits a pronounced metallacyclopropane character [**2**: δ C_2 40.2 (br d, J(CP) = 31.8 Hz), C_3 63.6 (dt, J(CP) = 31.5, 9.9 Hz); **3**: δ C_2 48.4 (dd, J(CP) = 26.3, 9.2 Hz), C_3 57.3 (dd, J(CP) = 21.5, 11.1 Hz)]. The distal thiophene ring in **3** undergoes regioselective insertion of rhodium into the unsubstituted C−S bond by reaction with a further equiv of **1** in refluxing THF. The resulting bimetallic complex $[(\text{triphos})\text{Rh}(\eta^3\text{-MeSC=CHCH=CH}_2)$(5,5′-BD-

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[7] $^{31}P\{^1H\}$ NMR (81.01 MHz, CD_2Cl_2, 20 °C): AMQX spin system, δ 31.1 (ddd, $J(P_AP_M)$ = 34.2 Hz, $J(P_AP_Q)$ = 29.1 Hz, $J(P_ARh)$ = 109.4 Hz, P_A), −0.8 (ddd, $J(P_MP_Q)$ = 36.2 Hz, $J(P_MRh)$ = 118.0 Hz, P_M), −4.1 (ddd, $J(P_QRh)$ = 106.0 Hz, P_Q). ^1H NMR (200.13 MHz, CD_2Cl_2, 20 °C): δ 6.70 (t, $J(H_4H_3)$ = 4.8 Hz, H_4), 3.15 (m, $J(H_{2'}Rh)$ = 2.2 Hz, $J(H_{2'}H_3)$ = 9.2 Hz, $H_{2'}$), 2.96 (m, $J(H_3Rh)$ = 1.0 Hz, $J(H_3H_2)$ = 7.4 Hz, H_3), 1.99 (m, $J(H_2Rh)$ = 1.4 Hz, H_2). $^{13}C\{^1H\}$ NMR (50.32 MHz, CD_2Cl_2, 20 °C): δ 63.6 (dt, J(CP) = 31.5, 9.9 Hz, C_3), 40.2 (br d, J(CP) = 31.8 Hz, C_2). Anal. Calcd (Found) for $C_{57}H_{49}P_3RhS_4$: C, 64.70 (63.55); H, 4.67 (4.88); Rh, 9.73 (9.53).

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[9] $^{31}P\{^1H\}$ NMR (81.01 MHz, CD_2Cl_2, 20 °C): AMQX spin system, δ 29.4 (t, $J(P_AP_M)$ = $J(P_AP_Q)$ = 37.9 Hz, $J(P_ARh)$ = 116.2 Hz, P_A), 3.9 (t, $J(P_MP_Q)$ = 37.9 Hz, $J(P_MRh)$ = 112.6 Hz, P_M), −6.4 (t, $J(P_QRh)$ = 103.1 Hz, P_Q). ^1H NMR (200.13 MHz, CD_2Cl_2, 20 °C): δ 7.6 (determined from selective $^1H\{^1H\}$ experiments, H_4), 3.49 (m, $J(H_3H_4)$ = 5.4 Hz, $J(H_3H_2)$ = 8.4 Hz, H_3), 2.65 (m, $J(H_{2'}Rh)$ = 2.3 Hz, $J(H_{2'}H_3)$ = 9.2 Hz, $J(H_{2'}H_2)$ = 1.8 Hz, $H_{2'}$), 2.33 (m, $J(H_2Rh)$ = 1.8 Hz, H_2), 1.70 (s, Me). $^{13}C\{^1H\}$ NMR (50.32 MHz, CD_2Cl_2, 20 °C): δ 149.2 (br s, C_4), 57.3 (dd, J(CP) = 21.5, 11.1 Hz, C_3), 48.4 (dd, J(CP) = 26.3, 9.2 Hz, C_2), 23.3 (br s, Me). Anal. Calcd (Found) for $C_{82}H_{72}BP_3RhS_4$: C, 70.74 (69.49); H, 5.21 (5.32); Rh, 7.39 (7.16).

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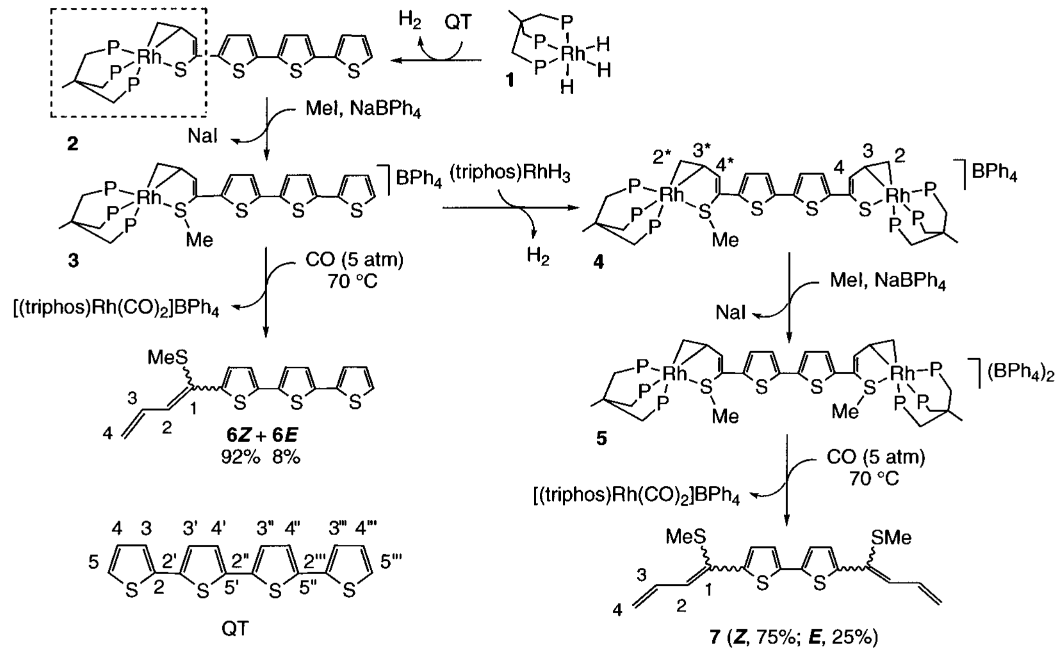
Scheme 1



Tyl)(η^3-SC=CHCH=CH$_2$)Rh(triphos)]BPh$_4$ (**4**) (BDTyl = 2,2′-bidithienyl) contains two chemically and magnetically inequivalent triphos ligands as shown by the ^{31}P{^{1}H} NMR spectrum, which consists of two distinct AMQX spin systems.[10] The ^{1}H NMR parameters of the CH$_2$ and CH groups in the thiobutadienyl and *S*-methylthiobutadienyl moieties of **4** are practically coincident with those of the same moieties in the precursors **2** and **3**. From **4**, the doubly S-methylated complex [(triphos)Rh(η^3-MeSC=CHCH=CH$_2$)(5,5′-BDTyl)(η^3-MeSC=CHCH=CH$_2$)Rh(triphos)]BPh$_4$ (**5**) is finally obtained by treatment with MeI, followed by metathetical reaction with NaBPh$_4$.[11] Again, the ^{1}H and ^{13}C NMR characteristics of **5** are quite comparable to those of the monomer **3**, while the symmetry of the molecule is shown by the presence of a unique AMQX pattern in the ^{31}P{^{1}H} NMR spectrum.

Compounds **3** and **5** are fully stable in both the solid state and solution. When their THF solutions are subjected to 5 atm of CO and then heated to 70 °C for 3 h, **3** and **5** quantitatively transform into the known dicarbonyl [(triphos)Rh(CO)$_2$]BPh$_4$,[5b,8,12] liberating the corresponding thio ligands. These are yellow solids that can be separated from the rhodium dicarbonyl complex by LC (silica column, diethyl ether). A comparison of their NMR characteristics to those of related 1-(alkylthio)-butadienes[5b,8,12,13] allows the identification of 5-[1-(methylthio)buta-1,3-diene]-2,2′:5′,2″-terthiophene (**6**), obtained from **3**, as a mixture of its *Z* and *E* stereoisomers (^{1}H NMR, **6*Z*** to **6*E*** ratio, 92:8).[14] The functionalized thiophene 5,5′-bis[1-(methylthio)buta-1,3-diene]-2,2′-bithiophene (**7**), obtained from **5**, is formed as a mixture of *ZZ*, *ZE*, and *EE* stereoisomers. The isomeric composition cannot be determined, however, as the ^{1}H NMR resonances of the *Z* (or *E*) butadienyl groups are identical in the *ZE* and *ZZ* (or *ZE* and *EE*) stereoisomers. ^{1}H NMR spectroscopy actually provides the ratio (75:25) between the total content of the *Z* and *E* configured double bonds in the molecule.[15]

The capability of the (triphos)rhodium–butadienethiolate moiety (dotted box in Scheme 1) to react with various electrophiles with different regiochemistry[16] and

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(10) ^{31}P{^{1}H} NMR (81.01 MHz, CD$_2$Cl$_2$, 20 °C): two AMQX spin systems, δ 31.1 (ddd, J(P$_A$P$_M$) = 34.7 Hz, J(P$_A$P$_Q$) = 29.6 Hz, J(P$_A$Rh) = 116.7 Hz, P$_A$), −0.6 (ddd, J(P$_M$P$_Q$) = 32.5 Hz, J(P$_M$Rh) = 118.4 Hz, P$_M$), −4.0 (ddd, J(P$_Q$Rh) = 107.8 Hz, P$_Q$), 29.2 (ddd, J(P$_{A*}$P$_{M*}$) = 39.0 Hz, J(P$_{A*}$P$_{Q*}$) = 36.4 Hz, J(P$_{A*}$Rh*) = 117.8 Hz, P$_{A*}$), 3.8 (ddd, J(P$_{M*}$P$_{Q*}$) = 36.5 Hz, J(P$_{M*}$Rh*) = 113.1 Hz, P$_{M*}$), −6.6 (t, J(P$_{Q*}$Rh*) = 103.2 Hz, P$_{Q*}$). ^{1}H NMR (200.13 MHz, CD$_2$Cl$_2$, 20 °C): δ 6.55 (m, J(H$_4$H$_3$) = 5.0 Hz, H$_4$), 3.17 (m, J(H$_{2'}$Rh) = 2.1 Hz, J(H$_{2'}$H$_3$) = 9.3 Hz, J(H$_{2'}$H$_2$) = 2.1 Hz, H$_{2'}$), 2.93 (m, J(H$_3$H$_2$) = 9.0 Hz, H$_3$), 2.0 (determined from selective ^{1}H{^{1}H} experiments, H$_2$), 7.6 (determined from selective ^{1}H-{^{1}H} experiments, H$_{4*}$), 3.49 (m, J(H$_{3*}$H$_{4*}$) = 5.3 Hz, J(H$_{3*}$H$_{2*}$) = 9.2 Hz, H$_{3*}$), 2.66 (m, J(H$_{2'*}$Rh*) = 2.0 Hz, J(H$_{2'*}$H$_{3*}$) = 9.1 Hz, J(H$_{2'*}$H$_{2*}$) = 2.0 Hz, H$_{2'*}$), 2.35 (m, J(H$_{2*}$Rh*) = 1.3 Hz, H$_{2*}$), 1.69 (s, Me). Anal. Calcd (Found) for C$_{123}$H$_{113}$BP$_6$Rh$_2$S$_4$: C, 69.62 (69.48); H, 5.37 (5.30); Rh, 9.70 (9.58).

(11) ^{31}P{^{1}H} NMR (81.01 MHz, CD$_2$Cl$_2$, 20 °C): AMQX spin system, δ 29.1 (t, J(P$_A$P$_M$) = 38.8 Hz, J(P$_A$P$_Q$) = 36.6 Hz, J(P$_A$Rh) = 116.3 Hz, P$_A$), 3.9 (t, J(P$_M$P$_Q$) = 35.5 Hz, J(P$_M$Rh) = 112.2 Hz, P$_M$), −6.2 (t, J(P$_Q$-Rh) = 102.7 Hz, P$_Q$). ^{1}H NMR (200.13 MHz, CD$_2$Cl$_2$, 20 °C): δ 7.6 (determined from selective ^{1}H{^{1}H} experiments, H$_4$), 3.49 (m, J(H$_3$H$_4$) = 5.3 Hz, J(H$_3$H$_2$) = 8.9 Hz, H$_3$), 2.66 (m, J(H$_{2'}$Rh) = 2.0 Hz, J(H$_{2'}$H$_3$) = 8.8 Hz, J(H$_{2'}$H$_2$) = 2.0 Hz, H$_{2'}$), 2.35 (m, J(H$_2$Rh) = 1.3 Hz, H$_2$), 1.69 (s, Me). ^{13}C{^{1}H} NMR (50.32 MHz, CD$_2$Cl$_2$, 20 °C): δ 149.7 (br s, C$_4$), 57.4 (dd, J(CP) = 20.2, 9.1 Hz, C$_3$), 48.6 (dd, J(CP) = 18.8, 9.2 Hz, C$_2$), 23.2 (br s, Me). Anal. Calcd (Found) for C$_{148}$H$_{136}$B$_2$P$_6$Rh$_2$S$_4$: C, 72.37 (72.11); H, 5.58 (5.51); Rh, 8.38 (8.28).

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(14) **6Z**. ^{1}H NMR (200.13 MHz, 20 °C): δ 7.4–6.9 (terthiophene hydrogens), 7.1 (masked by the terthiophene resonances, the chemical shift was determined by 2D COSY, H$_3$), 6.79 (br d, J(H$_2$H$_3$) = 10.9 Hz, H$_2$), 5.47 (ddd, J(H$_{4t}$H$_{4c}$) = 1.7 Hz, J(H$_{4t}$H$_3$) = 16.9 Hz, J(H$_{4t}$H$_2$) = 0.9 Hz, H$_{4t}$), 5.34 (ddd, J(H$_{4c}$H$_3$) = 10.2 Hz, J(H$_{4c}$H$_2$) = 0.8 Hz, H$_{4c}$), 2.28 (s, Me). ^{13}C{^{1}H} NMR (50.32 MHz, 20 °C): δ 147.0 (C$_1$), 133.8 (C$_3$), 128.5 (C$_2$), 120.5 (C$_4$), 17.8 (Me). **6E**. ^{1}H NMR (200.13 MHz, 20 °C): δ 7.4–6.9 (terthiophene hydrogens), 6.78 (dt, J(H$_3$H$_2$) = 10.9 Hz, J(H$_3$H$_{4t}$) = 17.0 Hz, J(H$_3$H$_{4c}$) = 10.2 Hz, H$_3$), 6.32 (br d, H$_2$), 5.32 (ddd, J(H$_{4t}$H$_{4c}$) = 1.7 Hz, J(H$_{4t}$H$_2$) = 0.9 Hz, H$_{4t}$), 5.12 (ddd, J(H$_{4c}$H$_2$) = 0.9 Hz, H$_{4c}$), 2.34 (s, Me). ^{13}C{^{1}H} NMR (50.32 MHz, 20 °C): δ 147.2 (C$_1$), 130.6 (C$_3$), 128.0 (C$_2$), 117.9 (C$_4$), 18.2 (Me).

(15) **7. *Z*-configured double bonds**. ^{1}H NMR (200.13 MHz, 20 °C): δ 7.2–6.9 (bithiophene hydrogens), 7.1 (dt partially masked by the dithiophene resonances, H$_3$), 6.78 (br d, J(H$_2$H$_3$) = 10.9 Hz, H$_2$), 5.49 (ddd, J(H$_{4t}$H$_{4c}$) = 1.7 Hz, J(H$_{4t}$H$_3$) = 16.7 Hz, J(H$_{4t}$H$_2$) = 0.9 Hz, H$_{4t}$), 5.34 (ddd, J(H$_{4c}$H$_3$) = 10.2 Hz, J(H$_{4c}$H$_2$) = 0.9 Hz, H$_{4c}$), 2.28 (s, Me). ***E*-configured double bonds**. ^{1}H NMR (200.13 MHz, 20 °C): δ 7.2–6.9 (bithiophene hydrogens), 6.78 (ddd, J(H$_3$H$_2$) = 11.1 Hz, J(H$_3$H$_{4t}$) = 16.8 Hz, J(H$_3$H$_{4c}$) = 10.1 Hz, H$_3$), 6.32 (br d, H$_2$), 5.32 (ddd, J(H$_{4t}$H$_{4c}$) = 1.7 Hz, J(H$_{4t}$H$_2$) = 0.9 Hz, H$_{4t}$), 5.13 (ddd, J(H$_{4c}$H$_2$) = 0.8 Hz, H$_{4c}$), 2.35 (s, Me).

the availability of a vast array of both metal fragments for the C−S bond scission step of thiophenes ([(dmpe)$_2$-Fe],[6a] [Cp*Rh(PMe$_3$)],[6b] [Cp*Ir],[6c] and [(triphos)IrH],[5c,d]) and oligothiophenes, taken altogether, confer a character of general methodology to the chemistry presented here. More importantly, the use of two different electrophiles in the two steps of electrophilic attack (Scheme 1) could allow the preparation of various noncentrosymmetric functionalized oligothiophenes, which are best suited for nonlinear optical activity.

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Supporting Information Available: Text giving experimental details of the synthesis and physicochemical characterization of the new complexes and thiophenes described in this paper (6 pages). Ordering information is given on any current masthead page.

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(16) Alkyl and acyl groups from the corresponding halides attack the sulfur atom, while the propensity of hard electrophiles such as H^+, CPh_3^+, and $C_7H_7^+$ is exclusively for the CH_2 carbon atom. See refs 5 and 12.