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Bond cleavage reactions in substituted thiophenes by a rhodium complex

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Dedicated to Professor Robert J. Angelici.

Abstract

The reactions of $(C_5Me_5)Rh(PMe_3)(Ph)H$ with 2-methoxythiophene, 3-methoxythiophene, 2-cyanothiophene, 3-cyanothiophene, 2-trimethylsilylthiophene, ethylenesulfide, trimethylenesulfide, and several polymethylthiophenes have been investigated. These thiophene derivatives give C–S and in one case C–H insertion products. Ethylene sulfide and trimethylene sulfide undergo ring opening or desulfurization.

Keywords: Hydrodesulfurization; C–S activation; C–H activation

1. Introduction

The hydrodesulfurization of petroleum is an important part of the processing of petroleum feedstocks to remove sulfur [1]. Derivatives of thiophenes, benzothiophenes, and dibenzothiophenes have been identified as some of the more difficult species to desulfurize [2]. Over the past 15 years, homogeneous transition metal systems have been used to provide structural and mechanistic models for key steps that may occur with the related heterogeneous catalysts [3]. The majority of these model studies have been performed with the parent thiophene/benzothiophene/dibenzothiophene substrates and their alkylated derivatives.

In these studies a variety of modes of interaction of small heterocycles with transition metal fragments has been elucidated. The fragment $[(C_5Me_5)Rh(PMe_3)]$ reacts with furan to give C–H activation products at the α-carbon [4], whereas thiophene formed a six-membered metallacycle [5]. Angelici found that benzothiophene coordinates to $[(C_5Me_5)Re(CO)_2]$ to form an equilibrium between η^2-C,C and η^1-S bound complexes, although no C–H or C–S cleavage was observed [6]. A few reported investigations with selenophene heterocycles and homogeneous transition metal complexes have focused on coordination modes of the selenophene ring. Choi and Angelici investigated substituted selenophenes with $[Cp'(CO)_2Re]$ ($Cp' = C_5H_5$ or C_5Me_5) and discovered an equilibrium between η^2-C,C and η^1-(*Se*) bound selenophenes, similar to results found with substituted thiophenes [7,8]. Studies by Sanger and Angelici investigated hindered rotation of η^5-coordinated thiophenes and selenophenes with chromium and manganese tricarbonyl complexes [9]. A study by Bianchini focused on the effects of functionalized thiophenes in reactions with [(triphos)RhH] [10].

As a continuation of our earlier experiments on the reactions of the $[(C_5Me_5)Rh(PMe_3)]$ fragment with thiophenes [5], several substituted thiophenes were examined which possess a variety of electronic and steric substituents. Electron donating and withdrawing groups were examined with methoxythiophenes and cyanothiophenes, respectively.

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The effects of substituents and their position on the thiophene ring will be discussed in light of previous regioselectivities. We had also observed an S-bound thiophene when tetramethylthiophene was reacted with $(C_5Me_5)Rh(PMe_3)PhH$ [11]. Further heating did not result in C–S insertion, but instead to decomposition. Insertion into the carbon sulfur bond had been observed with 2,5-dimethylthiophene, so a ''buttressing effect'' of methyl substituents in the 2 and 3 or 3 and 4 positions was proposed. To investigate further the effect of methyl substitution, several polymethyl-thiophenes were synthesized and their reactivity examined.

2. Experimental

2.1. General procedures

All manipulations were carried out under an N_2 atmosphere or on a high-vacuum line using Schlenk techniques. All solvents were distilled from dark purple solutions of sodium benzophenone ketyl under a nitrogen atmosphere. Reagent grade 2-methoxythiophene, 3-methoxythiophene, 2-cyanothiophene, 3-cyanothiophene, and 2-(trimethylsilyl)thiophene were purchased from Aldrich Chemical Company and were used without further purification, although each liquid was freeze–pump–thaw degassed (three cycles) prior to use. 2,3,4-Trimethylthiophene, 2,3,5-trimethylthiophene, and 3,4-dimethylthiophene were prepared according to literature methods [12]. Methylated thiophenes were purified on a Varian Aerograph Model 90P GC with an 8 ft prep column packed with a 10% SE-30 fluid phase on ChromosorbW acid washed 60/80 mesh support. ^1H (400 MHz), ^{31}P (162 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker AMX-400 and Avance 400 spectrometers.

2.2. Reaction of *1* with 2-methoxythiophene

2-Methoxythiophene (0.010 mL, 0.099 mmol) was added to an ampule containing 23 mg of **1** (0.059 mmol) in dry hexane (5 mL). The mixture was stirred at 64 °C for 48 h. After cooling, evaporation to dryness gave $(C_5Me_5)Rh[\kappa^2\text{-C,S–SCH=CH–CH=C(OMe)}]$ as a dark red solid. ^1H NMR (C_6D_6): δ 1.146 (d, $J = 10.5$ Hz, 9H), 1.642 (d, $J = 2.6$ Hz, 15H), 3.382 (s, 3H), 5.515 (dd, $J = 7.4$, 3.3 Hz, 1H), 5.865 (td, $J = 9.7$, 3.5 Hz, 1H), 6.055 (dd, $J = 9.5$, 7.3 Hz, 1H). ^{31}P NMR (C_6D_6): δ 11.58 (d, $J = 158.2$ Hz). ^{13}C NMR (C_6D_6): δ 9.21 (s, C_5Me_5), 15.33 (d, $J = 33.8$ Hz, PMe_3), 57.34 (s, OCH_3), 97.67 (s, CH), 99.78 (t, $J = 3.9$ Hz, C_5Me_5), 115.37 (s, CH), 121.10 (s, CH), 176.91 (dd, $J = 37.5$, 20.7 Hz, RhC).

2.3. Reaction of *1* with 3-methoxythiophene

3-Methoxythiophene (4.2 μL, 0.042 mmol) and **1** (10 mg, 0.021 mmol) were heated in dry C_6D_{12} in a resealable NMR tube with Teflon adapter at 63 °C for 23.5 h. Removal of solvent and excess 3-methoxythiophene followed by addition of dry C_6D_6 gave a dark red solution of $(C_5Me_5)Rh[\kappa^2\text{-C,S–SCH=CH–C(OMe)=CH}]$. X-ray quality single crystals were grown by slow evaporation of solvent at −20 °C in the glove box. ^1H NMR (C_6D_6): δ 1.006 (dd, $J = 10.3$, 0.7 Hz, 9H), 1.481 (d, $J = 2.8$ Hz, 15H), 3.647 (s, 3 H), 5.162 (dt, $J = 8.3$, 3.0 Hz, 1H, H-2), 6.184 (dd, $J = 10.0$, 2.8 Hz, 1H, H-4), 6.353 (dt, $J = 10.0$, 3.8 Hz, 1H, H-5). ^{31}P NMR (C_6D_6): δ 11.41 (d, $J = 155.6$ Hz). ^{13}C NMR (C_6D_6): δ 8.88 (s, C_5Me_5), 14.22 (d, $J = 35.4$ Hz, PMe_3), 50.29 (s, OCH_3), 98.0 (s, C_5Me_5), 122.94 (s,C–H4), 129.00 (s, C–H5), 165.8 (dd, $J = 34.9$, 25.2 Hz), Rh–C–H2, 166.0 (s, Rh–C–OCH_3). *Anal.* Calc. for $C_{18}H_{30}OSPRh$: C, 50.47; H, 7.06. Found: C, 50.67; H 6.92%.

2.4. Reaction of *1* with 2-cyanothiophene

Thermolysis of **1** (10 mg, 0.021 mmol) with 2-cyanothiophene (4.6 μL, 0.05 mmol) in dry C_6D_{12} at 67 °C for 15.5 h gave a single organometallic product. The product was formulated as insertion into the S–C(CN) bond by a ^{13}C JMOD experiment. X-ray quality single crystals were grown by slow evaporation of solvent at −20 °C in the glove box. ^1H NMR (C_6D_{12}): δ 1.035 (dd, $J = 10.6$, 0.8 Hz, 9H), 1.507 (d, $J = 2.9$ Hz, 15H), 6.152 (dd, $J = 5.0$, 3.8 Hz, 1H, H-4), 6.434 (dd, $J = 5.1$, 1.2 Hz, 1H, H-5), 6.732 (dd, $J = 3.8$, 1.2 Hz, 1H, H-3). ^{31}P NMR (C_6D_{12}): δ 9.014 (d, $J = 149.4$ Hz). ^{13}C NMR (acetone-d_6): δ 8.40 (s, C_5Me_5), 14.10 (d, $J = 35.0$ Hz, PMe_3), 100.55 (br s, C_5Me_5), 114.30(s, CN), 122.15 (s, CH), 128.70 (dd, $J = 35.0$, 24.0 Hz, Rh–C(CN)), 133.40 (s,C–H), 139.20 (s, C–H). *Anal.* Calc. for $C_{18}H_{27}NSPRh$: C, 51.07; H, 6.43; N, 3.31. Found: C, 51.71; H, 5.99; N, 2.83%.

2.5. Reaction of *1* with 3-cyanothiophene

A C_6D_{12} solution of **1** (10 mg, 0.021 mmol) was heated at 67 °C for 5.5 h with 3-cyanothiophene (5 μL, 0.05 mmol). Two C–S inserted products were observed. Further heating for 10 additional hours resulted in the disappearance of **1** and increase of these two products, maintaining the same 1:1 ratio. X-ray quality single crystals were grown by slow evaporation of solvent at −20 °C in the glove box. ^1H NMR ($(CD_3)_2CO$): δ 1.312 (d, $J =$ 10.6, 9H), 1.522 (d, $J = 11.4$, 9H), 1.636 (d, $J = 2.8$ Hz, 15H), 1.753 (d, $J = 2.7$ Hz, 15H), 5.526 (d, $J = 9.9$ Hz, 1H), 5.613 (s, 1H), 5.783 (s, 1H), 6.182 (dd, $J = 10.5$, 1.5 Hz, 1H), 6.393 (ddd, $J = 9.8$, 3.0, 0.8 Hz, 2H). ^{31}P NMR ($(CD_3)_2CO$): δ 6.23 (d, $J = 151.9$ Hz), 5.81 (d, $J = 146.0$ Hz). *Anal.* Calc. for $C_{18}H_{27}NSPRh$: C, 51.07; H, 6.43; N, 3.31. Found: C, 50.62; H, 6.33; N, 3.37%.

2.6. Reaction of *1* with 2-trimethylsilylthiophene

2-Trimethylsilylthiophene (0.20 mL, 1.21 mmol) was added to a hexane solution of **1** (30 mg, 0.076 mmol). The

mixture was stirred at 70 °C for 21 h during which time a color change to red was observed. The solvent and the excess 2-trimethylsilylthiophene were removed under vacuum. ^{1}H and ^{31}P NMR spectroscopic analysis showed a 3:2 mixture of a C–S insertion product and a C–H activation product. Upon heating the mixed products in C_6D_{12} at 70 °C for 9 days, the ratio of the two complexes begins to change with the C–H activation product decreasing, the C–S insertion product increasing and some $(C_5Me_5)Rh(PMe_3)_2$ decomposition product forming. For $(C_5Me_5)Rh[\kappa^2$-C,S–SC(SiMe$_3$)=CH–CH=CH], ^{1}H NMR (C_6D_{12}): δ 0.138 (s, 9H), 1.208 (dd, $J = 10.2$, 0.6 Hz, 9H), 1.607 (d, $J = 2.7$ Hz, 15H), 6.102 (d, $J = 6.7$ Hz, 1H), 6.429 (dt, $J = 7.6$, 3.0 Hz, 1H), 6.744 (ddt, $J = 8.6$, 3.7, 0.9 Hz, 1H). ^{31}P NMR (C_6D_{12}): δ 10.32 (d, $J = 162.2$ Hz). ^{13}C NMR (C_6D_{12}): δ −0.65 (s, SiMe$_3$), 8.98 (d, $J =$ 2.7 Hz, C_5Me_5), 14.91 (d, $J = 34.8$ Hz, PMe$_3$), 99.62 (t, $J = 3.8$ Hz, C_5Me_5), 125.90 (s, CH), 129.09 (s, CH), 133.69 (s, C), 141.03 (dd, $J = 31.0$, 22.9 Hz, RhCH). For $(C_5Me_5)Rh(PMe_3)$[5-(2-trimethylsilyl)-thienyl]H, ^{1}H NMR (C_6D_{12}): δ −12.791 (dd, $J = 47.7$, 29.2 Hz, 1H), 0.193 (s, 9H), 1.145 (dd, $J = 9.9$, 0.8 Hz, 9H), 1.817 (dd, $J = 2.2$, 0.8 Hz, 15H), 6.593 (d, $J = 3.1$ Hz, 1H), 6.984 (d, $J = 3.0$ Hz, 1H). ^{31}P NMR (C_6D_{12}): δ 8.58 (d, $J =$ 148.9 Hz). ^{13}C NMR (C_6D_{12}): δ 0.65 (s, SiMe$_3$), 10.08 (d, $J = 3.3$ Hz, C_5Me_5), 19.24 (d, $J = 32.6$ Hz, PMe$_3$), 98.23 (t, $J = 3.3$ Hz, C_5Me_5), 134.54 (s, CH), 134.97 (d, $J =$ 7.0 Hz, CH), 141.40 (s, C), 154.93 (dd, $J = 32.1$, 20.9 Hz, RhC).

2.7. Reaction of $(C_5Me_5)Rh(PMe_3)(3,5\text{-xylyl})H$ with 2,3,4-trimethylthiophene

A dry C_6D_{12} solution of $(C_5Me_5)Rh(PMe_3)$(3,5-xylyl)H (10 mg, 0.024 mmol) was heated at 47 °C with 2,3,4-trimethylthiophene (7 mg, 0.05 mmol) for 1 h. Two products were observed, one from activation of C–H5 and the other insertion into a C–S bond. Further heating resulted in decomposition. *C–H activation product:* ^{1}H NMR (C_6D_{12}): δ −12.722 (dd, $J = 48.3$, 28.3 Hz, 1H), 1.152 (d, $J = 10.2$ Hz, 9H), 1.834 (d, $J = 2.5$ Hz, 15H), 1.929 (s, 3H), 2.086 (s, 3H), 2.198 (s, 3H). ^{31}P NMR (C_6D_{12}): δ 10.00 (d, $J = 153.1$ Hz). *C–S insertion product:* ^{1}H NMR (C_6D_{12}): δ 1.323 (d, $J = 10.8$ Hz, 9H), 1.920 (d, $J = 2.5$ Hz, 15H), 1.920 (s, 3H), 2.095 (s, 3H), 2.297 (s, 3H), 6.875 (s, 1H). ^{31}P NMR (C_6D_{12}): δ 5.50 (d, $J = 154.8$ Hz).

2.8. Reaction of $(C_5Me_5)Rh(PMe_3)(3,5\text{-xylyl})H$ with 2,3,5-trimethylthiophene

Thermolysis of $(C_5Me_5)Rh(PMe_3)$(3,5-xylyl)H (10 mg, 0.024 mmol) and 2,3,5-trimethylthiophene (4 mg, 0.2 mmol) at 47 °C for 3.5 h gave two products in a 4:1 ratio, assigned as C–S insertion isomers. The major isomer was not identified as both products decomposed upon further heating. *Major product:* ^{1}H NMR (C_6D_{12}): δ 1.319 (dd, $J = 9.6$, 0.8 Hz, 9H), 1.696 (d, $J = 2.6$ Hz, 15H), 1.890 (s, 3H), 1.980 (s, 3H), 2.080 (s, 3H), 5.830 (br s, 1H). ^{31}P NMR (C_6D_{12}): δ 5.43 (d, $J = 168.0$ Hz). *Minor product:* ^{1}H NMR (C_6D_{12}): δ 1.285 (dd, $J = 7.1$, 0.8 Hz, 9H), 1.679 (d, $J = 2.7$ Hz, 15H), 2.155 (s, 3H), 2.710 (s, 3H), 3.140 (s, 3H), 5.380 (br s, 1H). ^{31}P NMR (C_6D_{12}): δ 6.98 (d, $J = 167.0$ Hz).

2.9. Reaction of $(C_5Me_5)Rh(PMe_3)(3,5\text{-xylyl})H$ with 3,4-dimethylthiophene

Reaction of a C_6D_{12} solution of $(C_5Me_5)Rh(PMe_3)$(3,5-xylyl)H (15 mg, 0.036 mmol) with 3,4-dimethylthiophene (16 mg, 1.3 mmol) at 47 °C for 6.5 h led to a 1.5:1 ratio of a C–H activation product to a C–S insertion product. Further heating for 6 h resulted in a decrease in the C–H activation product. The C–S insertion product increased, as did the decomposition product. *C–S insertion product:* ^{1}H NMR (C_6D_{12}): δ 1.180 (d, $J = 9.0$ Hz, 9 H), 1.597 (d, $J = 3.5$ Hz, 15H), 1.894 (s, 3H), 1.959 (s, 3H), 5.450 (br s, 1H), the other proton resonance was obscured. ^{31}P NMR (C_6D_{12}): δ 10.41 (d, $J = 163.0$ Hz). *C–H activation product:* ^{1}*H NMR* (C_6D_{12}): δ 1.790 (d, $J = 3.4$ Hz, 15H), 2.10 (s, 3H). ^{31}P NMR (C_6D_{12}): δ 9.96 (d, $J = 154.0$ Hz). The remaining resonances for the C–H activation product were obscured by decomposition products.

2.10. Competition reaction of **1** with thiophene/2,5-dimethylthiophene

About 0.20 g (0.051 mmol) **1** was dissolved in 4 mL hexane. 8.0 μL of thiophene (0.100 mmol) and 12 μL of 2,5-dimethylthiophene (0.105 mmol) were added to this solution separately via syringe. The reaction mixture was stirred in a glass ampule fitted with a Teflon stopcock for 20 h at 60 °C. After cooling, the solvent was removed and the dark red solid was dissolved in 0.5 mL C_6D_6. The C–S insertion products from thiophene and 2,5-dimethylthiophene were observed in a 2:1 ratio by ^{1}H NMR spectroscopy.

2.11. Reaction of **1** with ethylene sulfide

Ethylene sulfide (0.015 mL, 0.266 mmol) was added by syringe to a C_6D_{12} (0.5 mL) solution of **1** (20 mg, 0.051 mmol) in a resealable NMR tube equipped with a Teflon valve. A yellow solid precipitated immediately. Following reaction at room temperature for 24 h, the sample was examined by NMR spectroscopy. A ^{31}P NMR spectrum showed that only a single organometallic complex was formed at δ 6.72 (d, $J = 156.2$ Hz). The ^{1}H NMR spectrum showed a proton resonance at δ −2.876 (d, $J = 3.4$ Hz). The compound was identified as $(C_5Me_5)Rh(PMe_3)(C_6H_5)(SH)$ by comparison of its ^{1}H NMR spectrum with that of an authentic sample. Free ethylene (δ 5.265) and sulfur precipitate were also generated in this reaction. For $(C_5Me_5)Rh(PMe_3)(C_6H_5)(SH)$, ^{1}H NMR

(C_6D_{12}): δ −2.876 (d, $J = 3.4$ Hz, 1H), 1.280 (d, $J = 10.3$ Hz, 9H), 1.574 (s, 15 H), 6.709 (m, 1 H), 6.752 (m, 2H), 7.183 (br s, 2H).

2.12. Catalytic reaction of *10* with ethylene sulfide

Ethylene sulfide (0.030 mL, 0.500 mmol) was added by syringe to a C_6D_{12} (0.5 mL) solution of **10** (21.2 mg, 0.050 mmol) in a resealable NMR tube equipped with a Teflon valve. A yellow solid precipitated immediately. The reaction went to completion at room temperature in several days.

2.13. Reaction of *1* with trimethylene sulfide

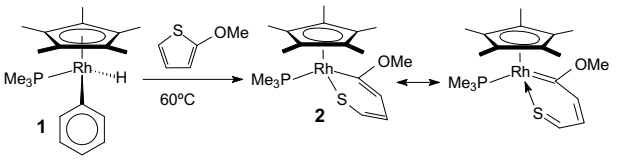
A cyclohexane solution of **1** (30 mg, 0.076 mmol) was treated with trimethylene sulfide (0.011 mL, 0.150 mmol). The solution was stirred for 3 h at room temperature. After removal of the solvent the residue was analyzed by NMR spectroscopy. A ^{31}P NMR spectrum revealed the presence of a single organometallic compound with a resonance at δ 8.45 (d, $J = 160.3$ Hz). This product was assigned as $(C_5Me_5)Rh(Ph)(SCH_2CH_2CH_3)$. ^{1}H NMR ($C_6D_6$): δ 0.987 (t, $J = 7.3$ Hz, 3H), 1.314 (d, $J = 10.0$ Hz, 9H), 1.577 (d, $J = 2.7$ Hz, 15H), 1.616 (m, 2H), 2.168 (t, $J = 14.6$ Hz, 2H), 6.751 (m, 1H), 6.805 (t, $J = 6.8$ Hz, 2H), 7.247 (d, $J = 7.6$ Hz, 2H). Further stirring the reaction mixture at room temperature for several days resulted in the formation of **10**.

3. Results and discussion

3.1. Reaction of $(C_5Me_5)Rh(PMe_3)(Ph)H$ with methoxythiophenes

The thermal reaction (60 °C) of $(C_5Me_5)Rh(PMe_3)(Ph)H$, **1**, with 2-methoxythiophene in hexane solution leads to the selective formation of a single C–S insertion product assigned as $(C_5Me_5)Rh(PMe_3)[\kappa^2$-C,S–SCH=CH–CH=C(OMe)], **2**. Evidence for this formulation in which the metal has inserted into the C–S bond on the more hindered side of the ring comes from examination of a ^{13}C JMOD (attached proton test) experiment. The carbon bound to rhodium is easily identified by its characteristic J_{Rh-C} and J_{P-C} couplings (shown by ^{31}P and ^{1}H decoupling). The ^{13}C JMOD experiment revealed the resonance at δ 176.91 (dd, $J = 37.5$, 20.7 Hz) as having opposite phase as the CH_3- and C–H resonances. This information identifies the carbon bound to rhodium as being C^2–OMe, i.e., with no attached hydrogens.[1]

The insertion into the substituted side of 2-methoxythiophene in **2** can be rationalized in terms of a Fischer-carbene stabilized resonance form, shown in Eq. (1). Heteroatom substituents are well known to stabilize electrophilic carbene complexes, and such a factor could be invoked in this case [13,14]. A similar methoxy carbene resonance form could stabilize the monomer and lead to cleavage of the S–C(OMe) bond, although this would formally invoke a 20e$^-$ species. Previous experiments with $(C_5Me_5)Rh(C_2H_4)$ and 2-methoxythiophene showed similar selective insertion behavior by cleaving the C–S bond on the side of the substituent forming a $(C_5Me_5)Rh[\kappa^2$-C,S–SCH=CH–CH=C(OMe)] 16 electron monomer, which was in equilibrium with *cis*- and *trans*-dimers [15].



(1)

Thermolysis of **1** with 3-methoxythiophene also gave a single C–S insertion product **3** identified by ^{1}H and ^{31}P NMR spectroscopies. A ^{1}H{^{31}P} experiment which revealed large ($J_{P-H} = 8.4$ Hz) and small ($J_{P-H} = 3.8$ Hz) phosphorus couplings to H-2 and H-5, respectively. Proton resonances of the inserted thiophene were identified through a series of homonuclear decoupling experiments. A large cis- coupling ($J_{H-H} = 10.0$ Hz) was observed between H-5 (δ 6.4) and H-4 (δ 6.2) while only a small w-coupling ($J_{H-H} = 3.0$ Hz) was seen between H-2 (δ 5.2) and H-4. A ^{13}C NMR spectrum showed a doublet of doublets resonance characteristic of the carbon bound to rhodium (δ 165.8, dd, $J = 34.9$, 25.2 Hz), and a ^{1}H–^{13}C heteronuclear correlation NMR experiment showed this carbon to be attached to H-2. This data is most consistent with insertion toward the methoxy substituent, $(C_5Me_5)Rh(PMe_3)[\kappa^2$-C,S–SCH=CH–C(OMe)=CH] (Eq. (2)). As proof of this geometry, a single crystal X-ray structure determination was made of **3**. As shown in Fig. 1, the indicated position of the methoxy group is confirmed.

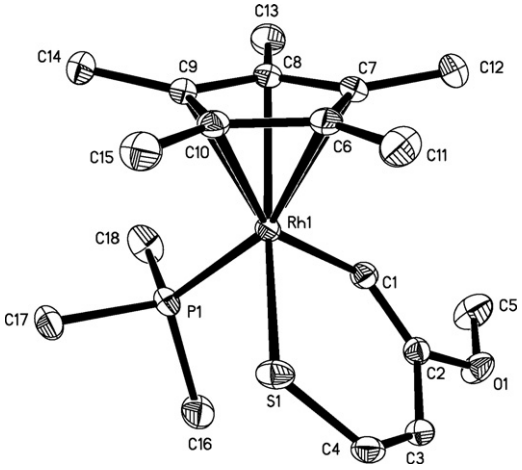
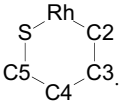
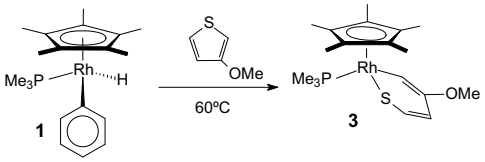


Fig. 1. ORTEP drawing of **3**. Ellipsoids are shown at the 30% probability level.

[1] The numbering scheme in the inserted complexes follows: 



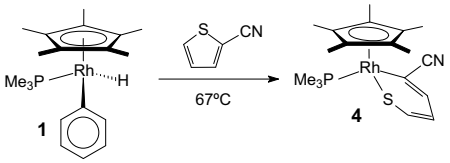
(2)

Previous results with the initial product from the reaction of 2-methylbenzothiophene with $[(C_5Me_5)Rh(PMe_3)]$ in which rhodium had inserted into the S-vinyl bond showed phosphorus coupling to the methyl hydrogens, i.e. the group bound to the rhodium α-carbon. The larger phosphorus coupling to H-2 in the 3-methoxythiophene complex suggests that rhodium has inserted between S and C-2. This insertion selectivity was confirmed by the heteronuclear correlation experiment.

Contrary to our observations for both 2-methoxy- and 3-methoxythiophene is a report by Bianchini and co-workers who reported C–S insertion toward the *unsubstituted* side in both molecules with [(triphos)RhH] [10]. These products, however, are hindered by the bulky triphos ligand, and selectivities reflect steric constraints which are absent in our $[(C_5Me_5)Rh(PMe_3)]$ system. In addition, the products eliminate a Rh–vinyl bond to generate a π-vinyl ligand, which may affect the thermodynamics of the cleavage reaction.

3.2. Reaction of $(C_5Me_5)Rh(PMe_3)(Ph)H$ with cyanothiophenes

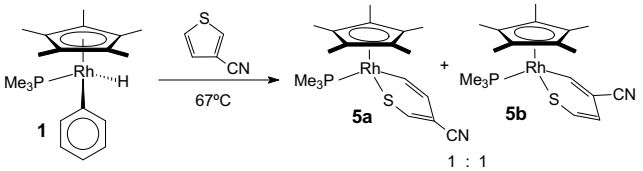
The reactions with 2- and 3-methoxythiophene suggested that π-donating groups on the thiophene ring direct insertion toward the side of the substituent. To examine an electron withdrawing substituent, 2- and 3-cyanothiophene were reacted with **1**. A C_6D_{12} solution of **1** was heated with 2-cyanothiophene at 67 °C for 15.5 h. A C–H activation product, present at early reaction times, was observed to go away with formation of a single C–S insertion product **4**. A ^{13}C JMOD experiment in acetone-d_6 showed the doublet of doublets resonance for the Rh–C with the same phase as the C_5Me_5 ring carbons, indicating that rhodium had inserted into the substituted C–S bond (Eq. (3)). This assignment was confirmed by the absence of any phosphorus coupling to thiophene ring protons. No change was seen in the coupling patterns of thiophene ring protons of the product during a $^1H\{^{31}P\}$ experiment, consistent with no hydrogens attached to α-carbon atoms.



(3)

The electron withdrawing cyano substituent would not stabilize a Fischer-carbene resonance form as in the case of 2-methoxythiophene. A strongly electron-withdrawing substituent could serve to reduce electron density at the α-carbon. Insertion of the rhodium from an S-bound intermediate has been envisioned as a nucleophilic attack of the electron rich rhodium on an α-carbon. This insertion could be driven to the substituted side by the removal of electron density by the cyano group, as was proposed in reactions of $[(C_5Me_5)Rh(PMe_3)]$ with 2-cyanodibenzothiophene and 2-trifluoromethyldibenzothiophene [16].

Thermolysis of **1** with 3-cyanothiophene gave two C–S inserted products in a 1:1 ratio, **5a** and **5b** (Eq. (4)). The reaction was followed periodically over 15 h at 67 °C and no change was observed in the 1:1 ratio. The electron withdrawing group in the 3 position does not appear to influence selectivities.



(4)

The proposed structures for **4** and **5a** were confirmed by single crystal X-ray diffraction (Fig. 2a and b). In both molecules, the thiophene ring is nearly planar. In **4**, the S1-Rh1-C1 plane is at an angle of 14.3° to the S1–C4–C3–C2–C1 plane. In contrast, the related dimethyl substituted derivative $(C_5Me_5)Rh(PMe_3)(\kappa^2\text{-}C,S\text{–}SCMe{=}CH\text{–}CH{=}CMe)$ is more strongly puckered (26°) due to steric interactions [5]. The structure of **5a** shows disorder in the possible orientation of the ring-opened thiophene, but a reasonable model can be obtained using the Shelx SAME instruction to constrain the two rings to have similar geometries.

3.3. Reaction of $(C_5Me_5)Rh(PMe_3)(Ph)H$ with trimethylsilylthiophene

Thermolysis of **1** with 2-(trimethylsilyl)thiophene at 70 °C for 21 h in dry C_6D_{12} gave two organometallic complexes **6a** and **6b** in a 3:2 ratio. The major product (δ 10.32) had a coupling constant characteristic of a C–S insertion

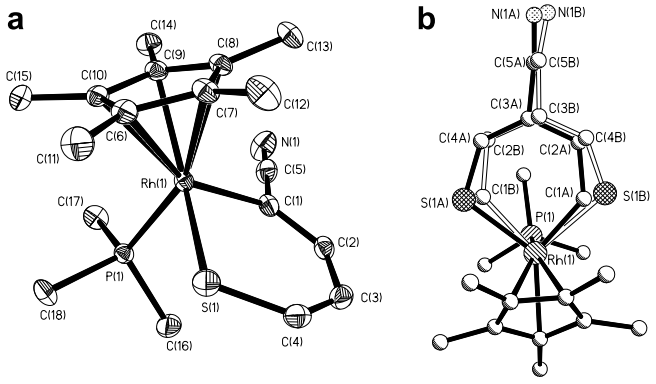
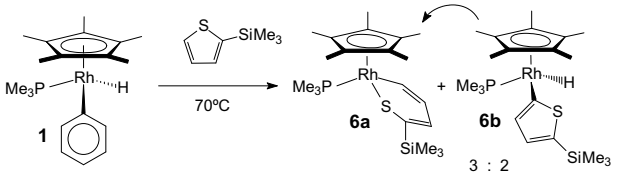


Fig. 2. (a) ORTEP drawing of **4**. Ellipsoids are shown at the 30% probability level. (b) Ball and stick drawing of **5a**. The two components (50/50) of the disorder model are shown.

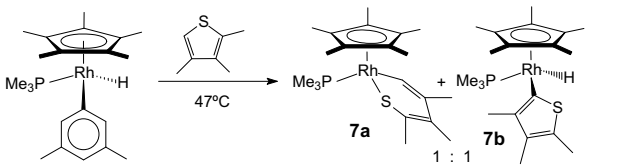
product with $J_{Rh-P} = 162.2$ Hz while the minor product displayed a coupling constant consistent with a C–H activation product, δ 8.58 ($J = 148.9$ Hz). A ^{13}C-JMOD NMR experiment revealed that the major product displayed a doublet of doublets at δ 141.03 ($J = 31.0$, 22.9 Hz), in phase with C–H and CH_3-resonances. This result identified the major product as C–S insertion away from the substituted side. A doublet of doublets at δ 154.93 ($J = 32.1$, 20.9 Hz) of opposite phase was also observed for the minor product, characteristic of activation of a thiophene ring C–H bond. A ^{1}H–^{1}H COSY NMR experiment allowed assignment of the minor product as the C–H activation of the C–H5 bond (Eq. (5)). Activation of the α-C–H bonds were previously observed as a kinetic product when $(C_5Me_5)Rh(PMe_3)H_2$ was photolyzed with thiophene [11]. Further heating at 70 °C for nine days resulted in a decrease in the C–H activation product with an increase in the C–S insertion product and the $(C_5Me_5)Rh(PMe_3)_2$ decomposition product.



(5)

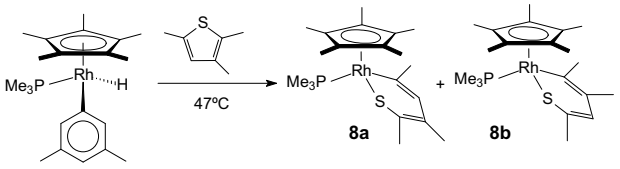
3.4. Reaction of $(C_5Me_5)Rh(PMe_3)(Ph)H$ with polymethylthiophenes

Treatment of a hexane solution of the more thermally labile $(C_5Me_5)Rh(PMe_3)$(3,5-xylyl)H with 2,3,4-trimethylthiophene at 47 °C for 3 h resulted in the formation of two products in a 1:1 ratio as observed by ^{1}H and ^{31}P NMR spectroscopies. One product (**7b**) was assigned as activation of the α-C–H bond by observation of a hydride resonance (δ −12.722, dd, $J = 48.3$, 28.3 Hz) in the ^{1}H NMR spectrum and typical ^{31}P NMR data (δ 10.00, dd, $J = 153.1$ Hz). The other product (**7a**) was assigned as arising from insertion into the S–C5 bond, away from the sterically hindered 2-methyl group based on previous evidence with 2-methylthiophene (Eq. (6)). (Reaction of **1** with 2-methylthiophene gave exclusive insertion into the unhindered C–S bond [5]). Unfortunately, further heating led to decomposition and full characterization was not possible.



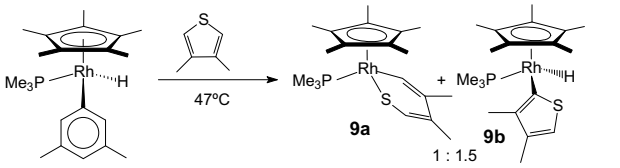
(6)

Thermolysis of $(C_5Me_5)Rh(PMe_3)$(3,5-xylyl)H with 2,3,5-trimethylthiophene in dry C_6D_{12} at 47 °C for 3.5 h resulted in the formation of two C–S inserted products in a 4:1 ratio (Eq. (7)). Further heating led to decomposition. Problems with thermal stability made thorough assignment of the products unrealizable. Earlier work with 2,5-dimethylthiophene, however, showed that insertion into the C–S bond was possible [5], although no insertion occurred with tetramethylthiophene due to the "buttressing effect" [11]. Consequently the major product is likely assigned structure **8a** due to the absence of a methyl group on C3.



(7)

3,4-Dimethylthiophene gave a 1:1.5 ratio of C–S to C–H activation products (**9a** and **9b**) when heated for 6.5 h at 47 °C with $(C_5Me_5)Rh(PMe_3)$(3,5-xylyl)H (Eq. (8)). The C–H activation product began to decrease upon heating for an additional 6 h with an increase in the amounts of the C–S inserted product and decomposition product $(C_5Me_5)Rh(PMe_3)_2$. Only one isomer is available for C–S insertion, and activation of the α-C–H bond is the assigned C–H activation product based on earlier thiophene kinetic studies [11]. 3,4-Dimethylthiophene gave more stable products than those of the two trimethylthiophenes. α-Methyl substituents have been known to destabilize C–S inserted products relative to thiophene [5] or benzothiophene [17], and are presumably contributing to the thermal instabilities seen in the reaction with 2,3,5-trimethylthiophene.



(8)

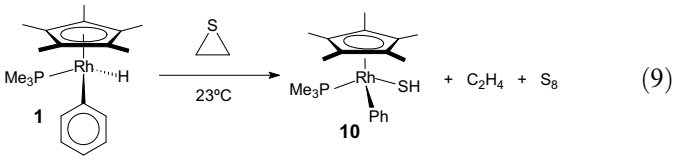
The reactivity patterns arising from study of these polymethylthiophenes shows a lower stability with increasing methyl substitution. The "buttressing effect" which may have prevented $[(C_5Me_5)Rh(PMe_3)]$ from inserting into the C–S bond of tetramethylthiophene may not only decrease insertion rates but also destabilize the C–S inserted products of di- or tri-methylthiophenes. In addition a competition between thiophene and 2,5-dimethylthiophene (1:1) in the thermal reaction with **1** at 60 °C showed a 2:1 preference for C–S activation of the less hindered substrate. Under these conditions, the C–S addition is irreversible. Consequently, α-methyl substitution has an effect on the kinetic selectivity as well.

3.5. Reaction of $(C_5Me_5)Rh(PMe_3)(Ph)H$ with ethylene sulfide and trimethylene sulfide

The previous experiments with a wide range of substrates have demonstrated that the rhodium complex is capable of insertion into C(sp^2)–S bonds of thiophenes in thermal reactions. The ability of the fragment $[(C_5Me_5)Rh(PMe_3)]$ to insert into these strong C–S bonds suggests that it might also be energetically capable of

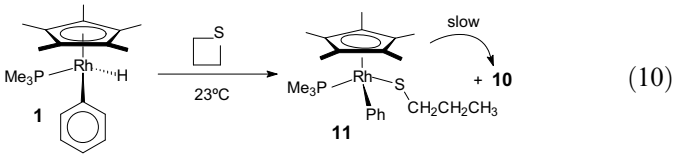
insertion into C(sp^3)–S bonds. Consequently, the thermal reactions of **1** with ethylene sulfide (C_2H_4S) and trimethylene sulfide (C_3H_6S) were examined.

Reaction of **1** with C_2H_4S in C_6D_{12} at room temperature gave an orange solution with concomitant formation of yellow precipitate, elemental sulfur. The ^{31}P NMR spectrum indicated that a single Rh(III) organometallic compound (δ 6.72, d, $J = 156$ Hz) was formed. A ^1H NMR spectrum showed resonances for free ethylene (δ 5.265) and for a Rh–SH proton at δ −2.876 (d, $J = 3.4$ Hz). The complex produced was assigned as (C_5Me_5)Rh(PMe_3)(Ph)(SH) (**10**) by comparison with an authentic sample (Eq. (9)) [18].



(9)

Room temperature reaction of **1** with trimethylene sulfide (C_3H_6S) in cyclohexane solution resulted in initially only the formation of an organometallic complex identified as (C_5Me_5)Rh(PMe_3)(Ph)($SCH_2CH_2CH_3$) (Eq. (10)). The assignment of the C–S insertion product was based on the ^{31}P NMR data, showing a doublet at δ 8.45 (d, $J = 160$ Hz). The ^1H NMR data showed resonances at δ 0.987 (t, $J = 7.3$ Hz, 3H), 1.616 (m, 2H) and 2.168 (t, $J = 14.6$ Hz, 2H) for the distinct opened chain hydrogens as well as doublets at δ 1.577 (d, $J = 2.7$ Hz, 15H) and 1.314 (d, $J = 10.0$ Hz, 9H) for the C_5Me_5 and PMe_3 protons. Further stirring the reaction mixture at room temperature for several days resulted in the formation of **10**.



(10)

Reaction with **1**-d_6 leads to formation of the product (C_5Me_5)Rh(PMe_3) (C_6D_5)($SCH_2CH_2CH_2D$). Reaction with a 60/40 mixture of **1** and **1**-d_6 produces a mixture of d_0, d_1, d_5, and d_6 products, indicating that crossover occurs during the addition of the C–S bond across the Rh–H(D) bond. While the mechanism was not examined in detail, a radical-based process could account for these results.

4. Summary

Insertion into the C–S bond of thiophene is highly influenced by both steric and electronic effects. Regiospecific insertion toward the substituted side of thiophene was seen with 2-methoxythiophene, 3-methoxythiophene, and 2-cyanothiophene. 3-Cyanothiophene showed the formation of two C–S insertion isomers in a 1:1 ratio while 2-trimethylsilylthiophene showed selective insertion away from the substituent as well as activation of the α-C–H bond.

Results with polymethylthiophenes indicate that presence of two or three methyl substituents on the thiophene ring do not prevent C–S insertion, but may destabilize the C–S inserted products. A single C–S insertion product was seen with 2,3,4-trimethylthiophene, presumably directed away from the α-methyl substituent. One C–H activation product was observed as well, likely activation at the α-carbon. Two C–S inserted products were seen with 2,3,5-trimethylthiophene in a 4:1 ratio. 3,4-Dimethylthiophenes shows single C–S inserted and C–H activation products. Small ring thiatanes lead to ring-opening additions and extrusion of sulfur by what may be radical processes. As all of the reactions that give mixtures of C–S insertion products do not change over time, the product formation can be either under kinetic control (i.e., C–S cleavage is irreversible) or under thermodynamic control, with fast equilibration of C–S bond cleavage products under the reaction conditions.

Acknowledgement

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Appendix A. Supplementary material

CCDC 659675, 658453, and 658454 contains the supplementary crystallographic data for **3**, **4** and **5a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2007.09.023.

References

[1] H. Topsøe, B.S. Clausen, F.E. Massoth, Hydrotreating Catalysis, Springer-Verlag, Berlin, 1996.
[2] T. Kabe, A. Ishihara, H. Tajima, Ind. Eng. Chem. Res. 31 (1992) 1577.
[3] R.A. Sanchez-Delgado, Organometallic Modeling of the Hydrodesulfurization and Hydronitrogenation Reactions, Kluwer Academic Publishers, Dordrecht, 2002.
[4] W.D. Jones, L. Dong, A.W. Myers, Organometallics 14 (1995) 855.
[5] W.D. Jones, L. Dong, J. Am. Chem. Soc. 113 (1991) 559.
[6] M.-G. Choi, R.J. Angelici, Organometallics 11 (1992) 3328.
[7] M.-G. Choi, R.J. Angelici, J. Am. Chem. Soc. 113 (1991) 5651, and references therein.
[8] R.J. Angelici, Coord. Chem. Rev. 105 (1990) 61.
[9] M.J. Sanger, R.J. Angelici, Organometallics 13 (1994) 1821, and references therein.
[10] C. Bianchini, M.V. Jiménez, A. Meli, F. Vizza, Organometallics 14 (1995) 3196.
[11] L. Dong, S.B. Duckett, K.F. Ohman, W.D. Jones, J. Am. Chem. Soc. 114 (1992) 151.
[12] M. Janda, J. Šrogl, I. Stibor, M. Nemec, P. Vopatrná, Synthesis (1972) 545.
[13] K.H. Dötz, H. Fischer, P. Hoffman, F.R. Kreissl, U. Schubert, K. Weiss, Transition Metal Carbene Complexes, Verlag Chemie, Deerfield Beach, FL, 1983.

[14] (a) C.P. Casey, in: M. Jones Jr., R.A. Moss (Eds.), Reactive Intermediates, vol. 2, Wiley, New York, 1981, p. 135;
(b) C.P. Casey, in: M. Jones Jr., R.A. Moss (Eds.), Reactive Intermediates, vol. 2, Wiley, New York, 1985, p. 150.
[15] W.D. Jones, R.M. Chin, J. Am. Chem. Soc. 114 (1992) 9851.
[16] A.W. Myers, W.D. Jones, Organometallics 15 (1996) 2905.
[17] A.W. Myers, W.D. Jones, S.M. McClements, J. Am. Chem. Soc. 117 (1995) 11704.
[18] W.D. Jones, V.L. Chandler, F.J. Feher, Organometallics 9 (1990) 164.