Homogeneous Reactions of Thiophenes with Transition Metals: A Modeling Approach for Elucidation of the Hydrodesulfurization Mechanism and an Effective Method for the Synthesis of Unusual Organosulfur Compounds

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Abstract: The fragment [(triphos)RhH], generated by thermolysis of (triphos)RhH$_3$ (**1**) in refluxing THF, reacts with thiophene (T) or benzo[*b*]thiophene (BT) to yield (triphos)Rh(η^3-SCH=CH—CH=CH$_2$) (**2**) and (triphos)Rh-{η^3-S(C$_6$H$_4$)CH=CH$_2$} (**3**), respectively [triphos = MeC(CH$_2$PPh$_2$)$_3$]. Compound **2** is selectively protonated at the terminal metal-bonded carbon atom (C$_2$) by HBF$_4$·OEt$_2$ to give, after anion exchange, the η^4-*C,C,C,S*-thiocrotonal-dehyde complex *anti*-[(triphos)Rh{η^4-SCHCHCH(CH$_3$)}]BPh$_4$ (**4**), which reacts with CO to yield [(triphos)Rh(CO)-{η^2-S=CH—CH=CH(CH$_3$)}]BPh$_4$ (**5**) and thermally isomerizes to *syn*-[(triphos)Rh{η^4-SCHCHCH(CH$_3$)}]BPh$_4$ (**6**) in solution. Complex **4** also reacts with MeI by selective delivery of Me$^+$ to the sulfur atom to give, after anion exchange, [(triphos)Rh(η^3-MeSCH=CH—CH=CH$_2$)]BPh$_4$ (**7**). On the other hand, Ph$_3$C$^+$ selectively attacks the C$_2$ carbon atom to yield [(triphos)Rh{η^4-SCHCHCH(CH$_2$CPh$_3$)}]PF$_6$ (**8**), whose structure has been determined by X-ray diffraction. Complex **8** crystallizes in orthorhombic space group $P2_12_12_1$ (no. 19) with $a = 10.834(6)$ Å, $b = 15.012$-(6) Å, $c = 39.902(9)$ Å, $Z = 4$, and $V = 6489.66$ Å^3. The cation [(triphos)Rh{η^4-SCHCHCH(CH$_2$CPh$_3$)}]$^+$ presents a distorted square pyramidal structure with one P atom occupying the apical position, while the remaining two P atoms plus the C6—S and the C7—C8 bonds occupy the basal sites; the C8 atom bears the trityl substituent. The vinylthiophenolate complex **3** is also selectively protonated at C$_2$ with HBF$_4$·OEt$_2$ to yield [(triphos)Rh{η^4-S(C$_6$H$_4$)-CH(CH$_3$)}]BPh$_4$ (**9**), which undergoes an intramolecular hydrogen shift from carbon to sulfur slowly at room temperature and rapidly in refluxing THF to produce [(triphos)Rh{η^3-HS(C$_6$H$_4$)CH=CH$_2$}]BPh$_4$ (**10**); complex (**10**) is deprotonated by *t*-BuOK to reform **3**. As in the case of **2**, MeI and Ph$_3$CPF$_6$ react with **3** by selective attack of S and C, yielding [(triphos)Rh{η^3-MeS(C$_6$H$_4$)CH=CH$_2$}]BPh$_4$ (**11**) and [(triphos)Rh{η^4-S(C$_6$H$_4$)CH(CH$_2$CPh$_3$)}]-PF$_6$ (**12**), respectively. All the rhodium complexes obtained by addition of electrophiles to **2** or **3** upon treatment with CO quantitatively transform into [(triphos)Rh(CO)$_2$]Y (Y = BPh$_4$, PF$_6$), liberating the thio ligands in solution. In this manner we have prepared the new organosulfur compounds 2-*n*-propenyl-4-methyl-4*H*-1,3-dithiine, 5,5,5-triphenyl-*trans*-2-pentenethial, 2-ethylidenecyclohexadienethione, and 2-(3,3,3-triphenylpropylidene)cyclohexa-dienethione and provided a convenient synthetic method for *cis*-1-(methylthio)butadiene, 2-vinylthiophenol, and *o*-(methylthio)styrene, which have been previously made by more complicated multistep syntheses. The chemistry herein described provides useful information on the fundamental aspects of hydrodesulfurization catalysis as well as a novel entry into the synthesis of organosulfur compounds.

Introduction

The hydrodesulfurization (HDS) reaction is of prime importance in the petroleum and coal industries. An intense effort has been devoted over the years to the fundamental understanding of the mechanisms which are operative in such processes over heterogeneous catalysts, particularly for simple model substrates such as thiophene (T) and benzo[*b*]thiophene (BT).[2] A mechanistic approach which continues to attract considerable attention is the development of the coordination chemistry of T and BT.[3] A rather large amount of information has been accumulating in recent times concerning the modes of bonding of such sulfur-containing molecules to metal centers in complexes, as well as the activation resulting therefrom. A particularly interesting mode of activation in relation to HDS mechanisms is the one involving C—S bond scission to produce thiametallacyclic species, which have been well characterized

in a number of cases. However, the reactivity of such ring-opened C$_4$H$_4$S and C$_8$H$_6$S fragments, which is key to the understanding of the pathways leading to sulfur extrusion, has not been studied in much detail.[4–7]

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We have previously reported ring-opening reactions of T and BT promoted by the [(triphos)Ir]$^+$ fragment, as well as some aspects of the reactivity of the resulting thiametallacycles leading to desulfurized and/or hydrogenated products [triphos = MeC-(CH$_2$PPh$_2$)$_3$].[4,5] In the present paper, we describe the interaction of the trihydride (triphos)RhH$_3$ (1) with T and BT to form the corresponding ring-opened derivatives, as well as the reactions of the resulting thiametallacycles with electrophiles such as H$^+$, CH$_3$$^+$, and Ph$_3C^+$, which contribute toward a better understanding of the HDS mechanisms. Furthermore, the various unsaturated ligands obtained in this manner may be easily released from the rhodium center, providing a novel synthetic route for organosulfur compounds which have not been previously reported or otherwise have been prepared by more complicated multistep procedures.

Experimental Section

General Procedure. All reactions and manipulations were routinely performed under a nitrogen atmosphere by using standard Schlenk techniques unless otherwise stated. Tetrahydrofuran (THF) and diethyl ether were distilled from LiAlH$_4$, CH$_2$Cl$_2$ from CaH$_2$, and *n*-heptane from sodium. The solvents were stored over molecular sieves and purged with nitrogen prior to use. Commercial thiophene (Aldrich) was purified as described previously.[8] Benzo[*b*]thiophene (Aldrich) was sublimed prior to use. Ph$_3$CPF$_6$ (Aldrich) was recrystallized from CH$_2$Cl$_2$/*n*-hexane prior to use. HBF$_4$·OEt$_2$ (85% solution in OEt$_2$), 5,5-dimethyl-1-pyrroline *N*-oxide, and TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) were purchased from Aldrich. All other chemicals were commercial products and were used as received without further purification. The trihydride (triphos)RhH$_3$ (1) was prepared as described in ref 9. All metal complexes were collected on sintered-glass frits and washed with appropriate solvents before being dried in a stream of nitrogen. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FT-IR spectrophotometer using samples mulled in Nujol between KBr plates. Deuterated solvents for NMR measurements were dried over molecular sieves. ^{1}H NMR spectra were obtained on a Bruker ACP 200 (200.13 MHz) spectrometer. ^{1}H NMR shifts are recorded relative to residual ^{1}H resonance in the deuterated solvent: CD$_2$Cl$_2$, δ 5.32; CDCl$_3$, δ 7.23. ^{13}C{^{1}H} NMR spectra were recorded on the Bruker ACP 200 instrument operating at 50.32 MHz. The ^{13}C{^{1}H} NMR shifts are given relative to the solvent resonance: CD$_2$Cl$_2$, δ 54.4; CDCl$_3$, δ 77.7. ^{31}P{^{1}H} NMR spectra were recorded on either a Varian VXR 300 or a Bruker ACP 200 spectrometer operating at 121.42 or 81.01 MHz, respectively. Chemical shifts are relative to external 85% H$_3$PO$_4$ with downfield values reported as positive. Broad band and selective ^{1}H{^{31}P} NMR experiments were carried out on the Bruker ACP 200 instrument equipped with a 5-mm inverse probe and a BFX-5 amplifier device. ^{13}C-DEPT, ^{1}H–^{13}C 2D-HETCOR, and ^{1}H–^{1}H 2D-COSY NMR experiments were conducted on the Bruker ACP 200 spectrometer. The computer simulation of NMR spectra was carried out with a locally developed package containing the programs LAOCN3[10] and Davins[11] running on a Compaq Deskpro 386/25 personal computer. The initial choices of shifts and coupling constants were refined by iterative least-squares calculations using experimental digitized spectra. The final parameters gave a satisfactory fit between

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experimental and calculated spectra, the agreement factor *R* being less than 1% in all cases. Conductivities were measured with an Orion Model 990101 conductance cell connected to a Model 101 conductivity meter. The conductivity data were obtained at sample concentrations of ca. 10^{-3} M in nitroethane solutions at room temperature. GC analyses were performed on a Shimadzu GC-14 A gas chromatograph equipped with a flame ionization detector and a 30 m (0.25-mm i.d., 0.25-*μ*m FT) SPB-1 Supelco fused silica capillary column. GC/MS analyses were performed on a Shimadzu QP 2000 apparatus equipped with a column identical to that used for GC analyses. Reactions under controlled pressure of carbon monoxide were performed with a Parr 4565 reactor equipped with a Parr 4842 temperature and pressure controller. The materials and the apparatus used for the electrochemical experiments have been described elsewhere.[12] Low-temperature cyclic voltammetric and macroelectrolysis tests were performed by using the Ag/AgCl reference electrode, the potential of which was −0.04 V *vs* SCE. Under the present experimental conditions, the ferrocenium/ferrocene couple was located at +0.45 V in dichloromethane solution.

Synthesis of (triphos)Rh(η^3-SCH=CH−CH=CH$_2$) (2). To a stirred suspension of (triphos)RhH$_3$ (1) (0.50 g, 0.68 mmol) in THF (40 mL) was added a 10-fold excess of thiophene (T) (0.57 mL), and then the mixture was heated at reflux temperature. Within a few minutes the solid dissolved. After ca. 3 h, the resulting yellow brown solution was concentrated to ca. 5 mL. Addition of ethanol (20 mL) led to precipitation of 2 as yellow microcrystals which were collected by filtration and washed with *n*-pentane, yield 72%. Anal. Calcd (found) for C$_{45}$H$_{44}$P$_3$RhS: C, 66.50 (66.21); H, 5.46 (5.43); Rh, 12.66 (12.41); S, 3.94 (3.73). IR: ν(C=C) 1560 (m) cm^{-1}.

Synthesis of (triphos)Rh{η^3-S(C$_6$H$_4$)CH=CH$_2$} (3). Complex 3 was synthesized in the same manner as described for 2 by starting from 1 (0.50 g, 0.68 mmol) and benzo[*b*]thiophene (BT) (0.91 g, 6.8 mmol). The precipitation was achieved by using a 1:3 mixture of diethyl ether and *n*-pentane, yield 85%. Anal. Calcd (found) for C$_{49}$H$_{46}$P$_3$RhS: C, 68.21 (68.11); H, 5.37 (5.26); Rh, 11.93 (11.84); S, 3.72 (3.58). IR: ν(C=C) 1556 (m) cm^{-1}.

***In Situ* NMR Studies.** The reactions of 1 with either T or BT were also carried out in sealed NMR tubes. Samples of 1 (ca. 0.03 mmol) were dissolved in THF-d_8 (0.7 mL) in a 5-mm NMR tube under nitrogen. After two freeze/thaw/pump cycles at −196 °C, 5 equiv of either T or BT was added. The tube was sealed under nitrogen and then introduced into an NMR probe at 20 °C. A reaction between 1 and T (or BT) occurred only above 65 °C. At this temperature, all 1 disappeared in ca. 3 h to give 2 (or 3) and H$_2$ (4.7 ppm). No intermediate species was observed by ^{31}P NMR in the course of the transformation of 1.

Synthesis of *anti*-[(triphos)Rh{η^4-SCHCHCH(CH$_3$)}]BPh$_4$ (4). Addition of a slight excess of HBF$_4$·OEt$_2$ (54 *μ*L, 0.27 mmol) to a stirred suspension of 2 (0.20 g, 0.25 mmol) in acetone (20 mL) at −20 °C led to dissolution of the solid complex to give a deep orange solution. After 2 h, NaBPh$_4$ (0.85 g, 0.25 mmol) in ethanol (5 mL) was added to the reaction mixture which was allowed to warm to room temperature. On portionwise addition of *n*-heptane (20 mL), orange microcrystals of 4 precipitated. They were filtered off and washed with *n*-pentane, yield 71%. Anal. Calcd (found) for C$_{69}$H$_{65}$BP$_3$RhS: C, 73.15 (72.87); H, 5.78 (5.68); Rh, 9.08 (8.88); S, 2.83 (2.69). Λ_M: 52 Ω^{-1} cm^2 mol^{-1}. Compound 4 is rather unstable in solution, slowly converting into its *syn* isomer 6 (see below). In THF at room temperature, ca. 10% conversion occurs in 24 h.

Synthesis of [(triphos)Rh(CO){η^2-S=CH−CH=CH(CH$_3$)}]BPh$_4$ (5). Carbon monoxide was bubbled through a CH$_2$Cl$_2$ (20 mL) solution of 4 (0.20 g, 0.18 mmol) for 5 min at room temperature. During this time the color of the solution changed from orange to yellow. After carbon monoxide was replaced with nitrogen, addition of ethanol (30 mL) and partial evaporation of the solvents under a brisk stream of nitrogen gave yellow crystals of 5 which were collected by filtration and washed with ethanol and *n*-pentane, yield 85%. Anal. Calcd (found) for C$_{70}$H$_{65}$BOP$_3$RhS: C, 72.42 (72.26); H, 5.64 (5.51); Rh, 8.86 (8.77); S, 2.76 (2.59). Λ_M: 54 Ω^{-1} cm^2 mol^{-1}. IR: ν(CO) 2035 (s) cm^{-1}.

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Synthesis of *syn*-[(triphos)Rh{η^4-SCHCHCH(CH$_3$)}]BPh$_4$ (6). A. A THF (60 mL) solution of **4** (0.20 g, 0.18 mmol) was heated at reflux temperature for ca. 3 h. During this time, there was a color change from orange to red. On concentration of the reaction mixture to 15 mL, red crystals of **6** precipitated. The reaction mixture was cooled to room temperature, and then ethanol (10 mL) was added to complete the precipitation of **6**, which was filtered off and washed with *n*-pentane, yield 76%. Anal. Calcd (found) for C$_{69}$H$_{65}$BP$_3$RhS: C, 73.15 (73.01); H, 5.78 (5.71); Rh, 9.08 (8.91); S, 2.83 (2.71). Λ_M: 56 Ω^{-1} cm^2 mol^{-1}.

B. A mixture of **2** (0.20 g, 0.25 mmol) and HBF$_4$·OEt$_2$ (54 μL, 0.27 mmol) in THF (60 mL) was heated at reflux temperature. After 3 h, NaBPh$_4$ (0.85 g, 0.25 mmol) in ethanol (30 mL) was added to the reaction mixture which was concentrated to ca. 20 mL under reduced pressure. Red crystals of **6** precipitated in 80% yield.

Synthesis of [(triphos)Rh(η^3-MeSCH=CH—CH=CH$_2$)]BPh$_4$ (7). A 3-fold excess of neat MeI (48 μL) was syringed into a stirred suspension of **2** (0.20 g, 0.25 mmol) in THF (20 mL) at room temperature. Within 10 min, the yellow solid dissolved to give a yellow solution. Addition of NaBPh$_4$ (0.85 g, 0.25 mmol) in ethanol (30 mL) and partial evaporation of the solvents under a steady stream of nitrogen gave yellow crystals of **7**. They were filtered off and washed with ethanol and *n*-pentane, yield 80%. Anal. Calcd (found) for C$_{70}$H$_{67}$-BP$_3$RhS: C, 73.30 (73.09); H, 5.89 (5.71); Rh, 8.97 (8.78); S, 2.79 (2.65). Λ_M: 50 Ω^{-1} cm^2 mol^{-1}. Compound **7** is thermally stable in refluxing THF.

Synthesis of [(triphos)Rh{η^4-SCHCHCH(CH$_2$CPh$_3$)}]PF$_6$ (8). Addition of a stoichiometric amount of Ph$_3$CPF$_6$ (0.10 g) to a yellow solution of **2** (0.20 g, 0.25 mmol) in CH$_2$Cl$_2$ (15 mL) at room temperature immediately gave a red solution. On addition of ethanol (30 mL) and partial evaporation of the solvents under a brisk flow of nitrogen, red crystals of **8** precipitated in 90% yield. Calcd (found) for C$_{64}$H$_{59}$F$_6$P$_4$RhS: C, 64.00 (63.88); H, 4.95 (4.87); Rh, 8.57 (8.41); S, 2.67 (2.53). Λ_M: 78 Ω^{-1} cm^2 mol^{-1}. Well-shaped crystals of formula **8**·CH$_2$Cl$_2$·0.5EtOH were obtained by slow crystallization of **8** from CH$_2$Cl$_2$ and ethanol. Anal. Calcd (found) for C$_{66}$H$_{64}$Cl$_2$F$_6$-O$_{0.5}$P$_4$RhS: C, 60.56 (60.31); H, 4.93 (4.81); Rh, 7.86 (7.68); S, 2.45 (2.23).

Synthesis of [(triphos)Rh{η^4-S(C$_6$H$_4$)CH(CH$_3$)}]BPh$_4$ (9). The synthesis of **9** follows that used for **4** except for the substitution of **3** (0.22 g, 0.25 mmol) for **2**. The product **9** was obtained as pink violet microcrystals, yield 73%. Anal. Calcd (found) for C$_{73}$H$_{67}$BP$_3$RhS: C, 74.11 (74.00); H, 5.71 (5.65); Rh, 8.70 (8.59); S, 2.71 (2.58). Λ_M: 54 Ω^{-1} cm^2 mol^{-1}. Compound **9** is rather unstable in room-temperature solutions, where it very slowly converts into its isomer **10** (see below).

Synthesis of [(triphos)Rh{η^3-HS(C$_6$H$_4$)CH=CH$_2$}]BPh$_4$ (10). A solution of **9** (0.30 g, 0.25 mmol) in THF (20 mL) was introduced in a Parr reactor and heated at 80 °C. After 18 h, the bomb was cooled to room temperature and the contents were transferred into a Schlenk-type flask. Addition of *n*-heptane (20 mL) and partial evaporation of the solvent under a steady stream of nitrogen led to the precipitation of **10** as a yellow green solid, yield 86%. Anal. Calcd (found) for C$_{73}$H$_{67}$BP$_3$RhS: C, 74.11 (73.98); H, 5.71 (5.61); Rh, 8.70 (8.61); S, 2.71 (2.66). Λ_M: 50 Ω^{-1} cm^2 mol^{-1}.

Reaction of 10 with *t*-BuOK. A 2-fold excess of *t*-BuOK (6 mg, 0.05 mmol) was added to an acetone-*d$_6$* (0.8 mL) solution of **10** (30 g, 0.025 mmol) at room temperature. Within 1 h, the color of the solution changed from green to yellow. The solution was transferred into an NMR tube. ^{1}H and ^{31}P{^{1}H} NMR spectra showed the complete conversion of **10** to **3**.

Synthesis of [(triphos)Rh{η^3-MeS(C$_6$H$_4$)CH=CH$_2$}]BPh$_4$ (11). Complex **11** was synthesized in the same manner as described for **7** except for the substitution of **3** (0.22 g, 0.25 mmol) for **2**, yield 85%. Anal. Calcd (found) for C$_{74}$H$_{69}$BP$_3$RhS: C, 74.25 (74.09); H, 5.81 (5.67); Rh, 8.59 (8.43); S, 2.68 (2.52). Λ_M: 54 Ω^{-1} cm^2 mol^{-1}. Compound **11** is thermally stable in refluxing THF.

Synthesis of [(triphos)Rh{η^4-S(C$_6$H$_4$)CH(CH$_2$CPh$_3$)}]PF$_6$ (12). The synthesis of **12** follows that used for **8** except for the substitution of **3** (0.22 g, 0.25 mmol) for **2** and by using 2-propanol as the precipitating solvent. The product **12** was obtained as green microcrystals in 70% yield. Anal. Calcd (found) for C$_{68}$H$_{61}$F$_6$P$_4$RhS: C, 65.28 (65.11); H, 4.91 (4.81); Rh, 8.22 (8.10); S, 2.56 (2.43). Λ_M: 76 Ω^{-1} cm^2 mol^{-1}.

Attempted Reactions of 2 (or 3) with Ph$_3$CPF$_6$ in the Presence of (A) Dry Air, (B) TEMPO, and (C) 5,5-Dimethyl-1-pyrroline *N*-Oxide. A. A stoichiometric amount of Ph$_3$CPF$_6$ (12 mg, 0.03 mmol) was added to a solution of **2** (or **3**) (0.03 mmol) in CD$_2$Cl$_2$ (1 mL) under dry air at room temperature. Immediately the color of the solution turned from yellow to red (or deep green). The ^{31}P{^{1}H} NMR spectrum of this solution showed the quantitative formation of **8** (or **12**).

B. A stoichiometric amount of Ph$_3$CPF$_6$ (12 mg, 0.03 mmol) was added to a solution of **2** (or **3**) (0.03 mmol) and TEMPO (10 mg, 0.06 mmol) in CD$_2$Cl$_2$ (1 mL) at room temperature. There was an immediate color change from yellow to red (or deep green). The ^{31}P{^{1}H} NMR spectrum of this solution showed the quantitative conversion of **2** (or **3**) to **8** (or **12**).

C. No reaction occurred when a ca. 1:1 mixture of Ph$_3$CPF$_6$ (12 mg, 0.03 mmol) and 5,5-dimethyl-1-pyrroline *N*-oxide (5 μL, 0.04 mmol) in CD$_2$Cl$_2$ (0.5 mL) was added to a solution of **2** (or **3**) (0.03 mmol) in CD$_2$Cl$_2$ (0.5 mL) at room temperature. Compound **2** (or **3**) was the only rhodium species detected in solution by ^{31}P{^{1}H} NMR spectroscopy.

Trapping of Ph$_3$C· with TEMPO. The trityl radical was generated by exhaustive electrolysis ($E_w = 0.05$ V, −20 °C) of a CH$_2$Cl$_2$ solution of Ph$_3$CPF$_6$ containing 0.1 M Bu$_4$NPF$_6$ as the supporting electrolyte. Addition of a stoichiometric amount of TEMPO to this solution caused the CV waves of the couple Ph$_3$C$^+$/Ph$_3$C· to disappear.

Reaction of Ph$_3$C$^+$ with 5,5-Dimethyl-1-pyrroline *N*-Oxide. The cyclic voltammogram of a CH$_2$Cl$_2$ solution (0.1 M Bu$_4$NPF$_6$, 20 °C) containing equivalent amounts of Ph$_3$CPF$_6$ and 5,5-dimethyl-1-pyrroline *N*-oxide showed the disappearance of the anodic and cathodic waves of the couple Ph$_3$C$^+$/Ph$_3$C·.

Carbonylation Reactions. In a typical experiment, a THF (50 mL) solution of the complex (ca. 0.3 mmol) was reacted with CO for 3 h under appropriate pressure and temperature conditions (see Table 3). A Parr reactor was employed for pressures higher than atmospheric. In the latter case, after being depressurized and vented under a nitrogen stream, the contents of the bomb were transferred into a Schlenk-type flask. The volatiles were then removed in vacuo at room temperature, and a portion of the residue was analyzed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopies. In all carbonylation reactions, [(triphos)Rh(CO)$_2$]Y^9 (Y = BPh$_4$, **13a**; Y = PF$_6$, **13b**) was the only rhodium complex detected in solution. The rest of the residue was chromatographed on a silica column (diethyl ether as eluant) to eliminate the rhodium complex. The diethyl ether phase was then concentrated to dryness in vacuo and the residue, dissolved in CDCl$_3$, appropriately characterized by ^{1}H and ^{13}C{^{1}H} NMR and GC/MS spectroscopies. In all cases, the yields of the organosulfur products were quantitative based on ^{1}H NMR integration with respect to *tert*-butyl methyl ether (δ 3.21, OMe; 1.20, CMe$_3$) as the internal standard. The assignment of the ^{1}H and ^{13}C-{^{1}H} NMR resonances for all the following organosulfur compounds has been made on the basis of the labeling shown in Table 3.

2-*n*-Propenyl-4-methyl-4*H*-1,3-dithiine (14).[13] ^{1}H NMR (CDCl$_3$, 20 °C): δ 5.83, dqd, 1H, H$_8$; 5.48, ddq, 1 H, H$_7$; 5.12, d, 1 H, H$_6$; 4.65, dd, 1H, H$_2$; 4.61, dd, 1H, H$_5$; 2.78, qd, 1H, H$_4$; 1.74, dd, 3H, H$_9$; 0.98, d, 3H, H$_{10}$; ^3J(H$_2$H$_7$) = 8.8 Hz, ^4J(H$_2$H$_8$) = 0.7 Hz, ^3J(H$_7$H$_8$) = 15.0 Hz, ^4J(H$_7$H$_9$) = 1.6 Hz, ^3J(H$_8$H$_9$) = 6.4 Hz, ^3J(H$_4$H$_5$) = 0.7 Hz, ^3J(H$_4$H$_{10}$) = 7.1 Hz, ^3J(H$_5$H$_6$) = 6.1 Hz. ^{13}C{^{1}H} NMR (CDCl$_3$, 20 °C): δ 134.2, C$_6$; 126.2, C$_7$; 124.7, C$_8$; 121.5, C$_5$; 54.9, C$_2$; 43.8, C$_4$; 18.7, C$_{10}$; 15.9, C$_9$. Compound **14** could not be separated from a minor species (ca. 10%). On the basis of its ^{1}H NMR resonances, although poorly resolved and in some cases partially masked by those of **14**, the latter compound was tentatively identified as the isomer 3-*n*-propenyl-4-methyl-4*H*-1,2-dithiine.

2-Ethylidenecyclohexadienethione (15). ^{1}H NMR (CDCl$_3$, 20 °C): δ 7.3−7.1, m, 4H, H$_3$−H$_6$; 3.83, q, 1H, H$_7$; 1.57, d, 3H, H$_8$; ^3J(H$_7$H$_8$) = 7.5 Hz. ^{13}C{^{1}H} NMR (CDCl$_3$, 20 °C): δ 207.4, C$_1$; 141.3, CH; 138.7, CH; 131.8, CH; 131.2, CH; 130.1, C$_2$; 124.1, C$_7$; 15.9, C$_8$. GC/MS: EIMS (70 eV) [*m/e* (%)]: 136 (10) M$^+$, 135 (100) M − H$^+$, 91 (48) PhCH$_2$$^+$.

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Table 1. $^{31}P\{^1H\}$ NMR Spectral Data for the New Complexes[a]

complex	pattern	chem shift, ppm[b]			coupling const, Hz					
		δA	δM	δQ	J(AM)	J(AQ)	J(MQ)	J(Arh)	J(MRh)	J(QRh)
2	AMQX	31.4	0.2	−4.0						
	AMQX[c]	31.4	−0.3	−3.5	34.6	29.1	39.4	108.3	119.4	106.4
3	AMQX	30.7	0.1	−7.7	34.5	30.5	46.3	108.3	116.7	106.3
4	A₃X	10								
	AMQX[d]	32.0	10.9	−11.3	39.3	8.1	20.6	107.4	145.6	102.6
5	AMQX	10.5	2.0	−1.1	37.4	13.3	41.6	121.1	85.6	93.8
6	AMQX	29	7	−1						
	AMQX[e]	28.7	6.5	−0.3	29.3	4.8	23.6	111.9	138.8	120.0
7	AMQX	30.0	4.2	−8.1						
	AMQX[c]	30.0	4.2	−8.5	36.8	38.0	34.7	115.4	114.1	102.0
8	AMQX	28	4	3						
	AMQX[e]	28.3	4.3	2.0	29.0	4.4	26.1	112.1	137.5	121.3
9	AMQX	33.4	10.5	−4.9						
	AMQX[d]	32.7	10.9	−4.7	34.3	5.5	31.6	167.3	91.6	93.2
10	AMQX	30.1	5.9	−10.0						
	AMQX[c]	30.5	6.5	−10.7	34.3	40.3	40.3	113.3	112.3	103.0
11	AMQX	30.0	5.2	−8.4						
	AMQX[c]	30.0	5.5	−9.3	35.4	39.0	37.5	113.5	112.3	103.8
12	AMQX	34.3	22.1	−17.4	46.9	10.9	21.8	171.1	111.7	89.9

[a] All spectra were recorded at 20 °C in CD_2Cl_2 solutions unless otherwise stated. [b] The chemical shifts (δ's) are relative to 85% H_3PO_4; downfield values are assumed as positive. [c] At −10 °C. [d] At −40 °C. [e] At −20 °C.

2-Vinylthiophenol (16).[14] ^1H NMR ($CDCl_3$, 20 °C): δ 7.6−7.0, m, 4H, H_3−H_6; 7.1, masked by H_3−H_6, the chemical shift was determined from a H−H decoupling experiment, H_7; 5.80, dd, 1H, H_8; 5.35, dd, 1H, $H_{8'}$; 3.41, s, 1H, SH; $^2J(H_8H_{8'}) = 1.1$ Hz, $^3J(H_8H_7) = 17.4$ Hz, $^3J(H_{8'}H_7) = 11.2$ Hz. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 139.3, C_2; 135.5, C_7; 131.0, C_6; 130.4, C_1; 128.7, C_5; 127.2, C_3; 126.7, C_4; 116.3, C_8. GC/MS (EIMS, 70 eV) [m/e (%)]: 136 (10) M⁺, 135 (100) M − H⁺, 91 (48) $PhCH_2$⁺.

cis-1-(Methylthio)butadiene (17).[15] ^1H NMR ($CDCl_3$, 20 °C): δ 6.59, 1H, H_3; 6.12, 1 H, H_2; 6.00, 1 H, H_1; 5.22, 1H, H_5; 5.15, 1H, H_4; 2.32, s, 3H, SMe; $^2J(H_5H_4) = 1.5$ Hz, $^3J(H_5H_3) = 16.8$ Hz, $^3J(H_4H_3) = 11.3$ Hz, $^3J(H_3H_2) = 9.5$ Hz, $^3J(H_2H_1) = 9.5$ Hz.

o-(Methylthio)styrene (18).[16] ^1H NMR ($CDCl_3$, 20 °C): δ 7.6−7.0, m, 4H, H_3−H_6; 7.1, masked by H_3−H_6, the chemical shift was determined from a H−H decoupling experiment, H_7; 5.71, dd, 1H, H_8; 5.35, dd, 1H, $H_{8'}$; 2.47, s, 3H, SMe; $^2J(H_8H_{8'}) = 1.4$ Hz, $^3J(H_8H_7) = 17.4$ Hz, $^3J(H_{8'}H_7) = 11.0$ Hz. GC/MS (EIMS, 70 eV) [m/e (%)]: 150 (25) M⁺, 135 (100) M − Me⁺, 91 (48) $PhCH_2$⁺.

5,5,5-Triphenyl-*trans*-2-pentenethial (19). ^1H NMR ($CDCl_3$, 20 °C): δ 9.27, d, 1H, H_1; 7.3−7.1, m, 15H, H_7−H_9; 6.67, dt, 1H, H_3; 6.04, ddt, 1H, H_2; 3.68, dd, 2H, H_4; $^3J(H_1H_2) = 7.9$ Hz, $^3J(H_2H_3) = 15.6$ Hz, $^4J(H_2H_4) = 1.5$ Hz, $^3J(H_3H_4) = 6.7$ Hz. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 194.1, C_1; 156.1, C_3; 146.1, C_{Ph}; 129.7, CH_{Ph}; 128.8, CH_{Ph}; 127.1, CH_{Ph}; 126.1, C_2; 55.6, C_5; 44.7, C_4.
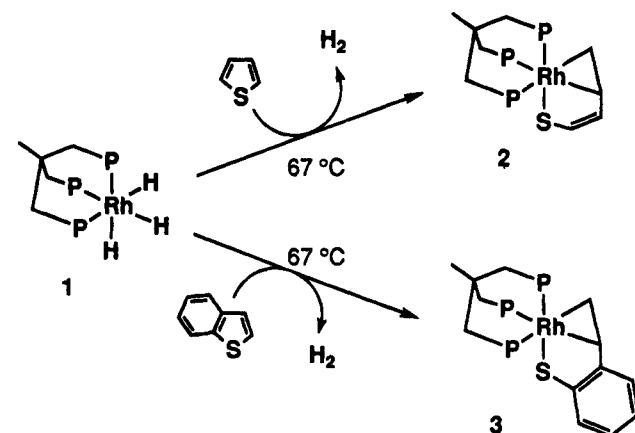
2-(3,3,3-Triphenylpropylidene)cyclohexadienethione (20). ^1H NMR ($CDCl_3$, 20 °C): δ 7.5−7.1, Ph_3C phenyl protons; 7.1, partially masked by Ph_3C phenyl protons, the chemical shift was determined from a H−H decoupling experiment, H_5−H_6; 6.76, td, 1H, H_4; 5.28, dt, 1H, H_3; 3.95, m, 2H, H_7−$H_{8'}$; 2.71, m, 1H, H_8; $^2J(H_8H_{8'}) = 14.2$ Hz, $^3J(H_8H_7) = -5.2$ Hz, $^3J(H_{8'}H_7) = -3.3$ Hz, $^4J(H_7H_3) = 1.3$ Hz, $^3J(H_4H_3) = 7.9$ Hz, $^4J(H_5H_3) = 1.3$ Hz, $^3J(H_5H_4) = 7.6$ Hz, $^4J(H_6H_4) = 1.4$ Hz, $^3J(H_6H_5)$ not determined. The H_7, H_8, and $H_{8'}$ protons constitute an ABX system. Their coupling constants were obtained by computer simulation of the experimental spectrum. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 206.8, C_1; 147.5, C_7; 146.7, C_{Ph}; 139.0, C_5; 130.8, C_2; 129.7, CH; 129.1, CH; 128.8, CH_{Ph}; 127.5, CH_{Ph}; 126.4, CH_{Ph}; 122.9, C_6; 57.8, C_9; 43.6, C_8.

X-ray Data Collection and Structure Determination of 8·CH_2-Cl_2·0.5EtOH. Intensities of a crystal sealed in a capillary with its solvent were collected on a Philips PW1100 FEBO diffractometer. A set of 25 carefully centered reflections having $8 < \theta < 13°$ were used to determine the cell constants. Three standard reflections were

Scheme 1

measured every 200 reflections for the orientation and intensity control. During data collection no decay of the specimen was noticed. Intensity data were corrected for Lorentz−polarization effects. Atomic scattering factors were those reported by Cromer and Waber[17] with an anomalous dispersion correction taken from ref 18. An empirical absorption correction was applied using the program DIFABS[19] with transmission factors in the range 0.83−1.21. All the computational work was carried out on a DIGITAL DEC 5000/200 workstation using the program SHELX76.[20] The programs PARST[21] and ORTEP[22] were also used. Crystallographic details are reported in Table 4. The structure was solved by using the heavy atom technique, and all of the non-hydrogen atoms were found through a series of F_o Fourier maps. Hydrogen atoms were introduced at calculated positions. Phenyl rings were treated as rigid bodies. Refinement was done by full-matrix least-squares calculations, initially with isotropic thermal parameters. In the last least-squares cycles, anisotropic thermal parameters were used for rhodium and phosphorus atoms. At the last stage of the refinement, two solvent molecules of dichloromethane and one of ethanol were detected; population factors of 0.5 were assigned to all the atoms. Due to disorder, the oxygen atom of ethanol was treated as a carbon atom.

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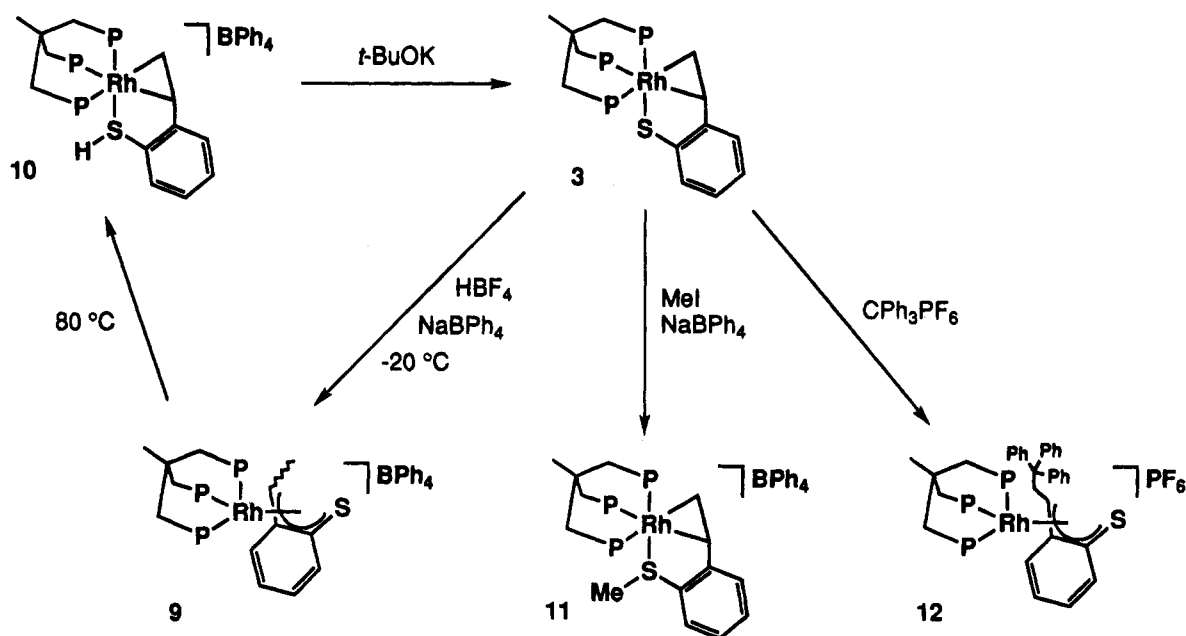
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Scheme 2
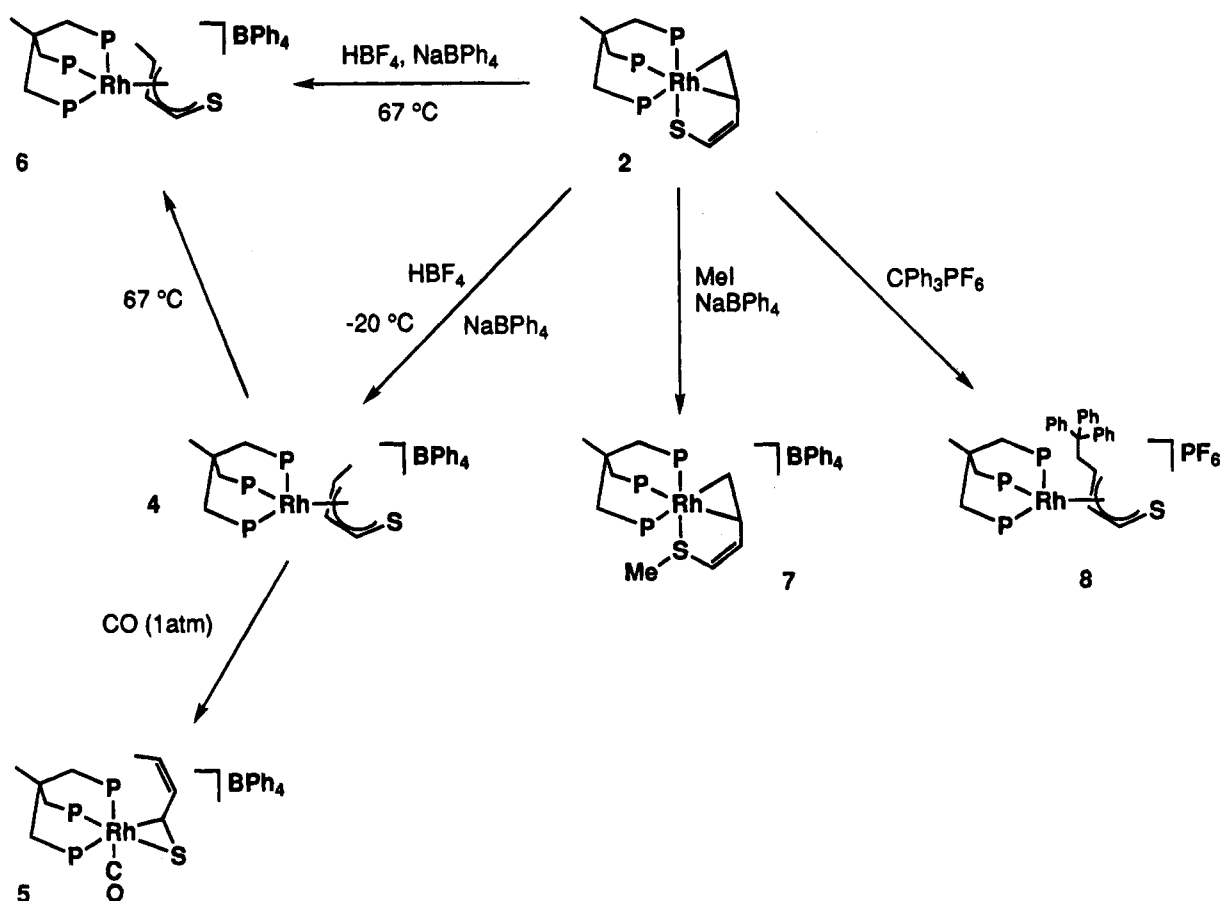
Scheme 3

The poor quality, the low number of observed reflections, the split images of the PF_6 anion, and the disordered solvent molecules are all responsible for the relative high R factors at the end of the refinement.

Calculations. Molecular orbital calculations were carried out by the extended Hückel method[23] with the parameters listed in Table 6. The off-diagonal elements were calculated by using the weighted Wolsberg—Helmholz formula with a distance-dependent Hückel constant.[24]

Results

The preparations and the principal reactions of the complexes described in this paper are illustrated in Schemes 1—3. Selected NMR spectral data for the metal complexes are collected in Table 1 ($^{31}P\{^1H\}$ NMR) and Table 2 (^1H, $^{13}C\{^1H\}$ NMR). ^{13}C-DEPT, $^{13}C-^1H$ 2D HETCOR, and $^1H-^1H$ 2D COSY spectra allowed the total and unequivocal assignment of all hydrogen
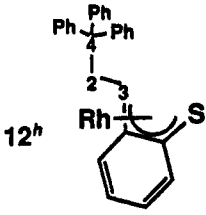
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Table 2. Selected NMR Spectral Data for the New Complexes[a]

		^{1}H NMR		^{13}C{^{1}H} NMR
complex	assign	δ (multiplicity, J)[b,c]	assign	δ (multiplicity, J)[b]
2	H$_4$	5.98 (m, ^{3}J(H$_4$Rh) = 1.0, ^{3}J(H$_4$H$_3$) = 4.5)	C$_3$	65.7 (dt, ^{2}J(CP) = 33.8, 9.2, ^{1}J(CRh) = 9.2)
	H$_5$	5.87 (m, ^{3}J(H$_5$Rh) = 2.0, ^{3}J(H$_5$H$_4$) = 6.1)	C$_2$	40.8 (br d, ^{2}J(CP) = 32)
	H$_3$	3.26 (m, ^{2}J(H$_3$Rh) = 1.1, ^{3}J(H$_3$H$_2$) = 7.5)	C$_4$	d
	H$_{2'}$	2.86 (m, ^{2}J(H$_{2'}$Rh) = 2.0, ^{3}J(H$_{2'}$H$_3$) = 9.3)	C$_5$	d
	H$_2$	1.63 (m, ^{2}J(H$_2$Rh) = 1.7, ^{2}J(H$_{2'}$H$_2$) = 0.5)		
3	H$_3$	3.43 (m, ^{2}J(H$_3$Rh) = 1.2, ^{3}J(H$_3$H$_{2'}$) = 9.2)	C$_3$	63.6 (dt, ^{2}J(CP) = 33.1, 9.1, ^{1}J(CRh) = 9.1)
	H$_{2'}$	3.26 (m, ^{2}J(H$_{2'}$Rh) = 2.1, ^{2}J(H$_{2'}$H$_2$) = 0.5)	C$_2$	39.4 (br d, ^{2}J(CP) = 38.9)
	H$_2$	1.82 (m, ^{2}J(H$_2$Rh) = 1.5, ^{3}J(H$_2$H$_3$) = 7.7)		
4	H$_5$	6.93 (m, ^{3}J(H$_5$H$_4$) = 4.5)	C$_5$	112.1 (br d, ^{2}J(CP) = 3)
	H$_4$	5.98 (m, ^{3}J(H$_4$H$_3$) = 8.0, ^{2}J(H$_4$Rh) = 1.5)	C$_4$	100.7 (br s)
	H$_3$	2.3[e]	C$_3$	63.6 (qd, ^{2}J(CP) = 15.3, ^{1}J(CRh) = 8.1)
	H$_2$	1.93 (dq, ^{3}J(H$_2$H$_3$) = 6.9, ^{4}J(H$_2$P) = 4.8)	C$_2$	15.1 (s)
5	H$_4$	6.07 (br t, ^{3}J(H$_4$H$_3$) = 10.7, ^{3}J(H$_4$H$_5$) = 11.5)	C$_{CO}$	196.8 (dq, ^{1}J(CRh) = 58.2, ^{2}J(CP) = 22.7)
	H$_3$	5.63 (m, ^{3}J(H$_3$H$_2$) = 7.1)	C$_4$	139.8 (d, ^{2}J(CP) = 6.2)
	H$_5$	4.56 (br d, ^{2}J(H$_5$Rh) = 1.2)	C$_3$	125.6 (d, ^{2}J(CP) = 9.5)
	H$_2$	1.47 (m, ^{4}J(H$_4$H$_2$) = 1.7)	C$_5$	72.2 (dd, ^{1}J(CRh) = 12.0, ^{2}J(CP) = 31.8)
			C$_2$	13.8 (br s)
6	H$_5$	6.42 (qt, ^{3}J(H$_5$H$_4$) = 4.1)	C$_5$	108.1 (br s)
	H$_4$	5.99 (dd, ^{3}J(H$_4$H$_3$) = 10.3)	C$_4$	96.8 (br s)
	H$_3$	3.88 (qt, ^{3}J(H$_3$H$_2$) = 6.4)	C$_3$	77.7 (m)
	H$_2$	0.01 (dq, ^{4}J(H$_2$P) = 4.9)	C$_2$	13.6 (s)
7	H$_4$	7.5[f]	C$_4$	156.0 (br s)
	H$_5$	5.71 (m, ^{3}J(H$_5$H$_4$) = 6.6)	C$_5$	117.0 (br d, ^{3}J(CP) = 11.6)
	H$_3$	3.52 (m, ^{3}J(H$_3$H$_4$) = 6.0, ^{3}J(H$_3$H$_2$) = 7.6, ^{2}J(H$_3$Rh) = 2.0)	C$_3$	59.3 (dd, ^{2}J(CP) = 21.8, 8.9)
	H$_{2'}$	2.34 (m, ^{3}J(H$_{2'}$H$_3$) = 9.1, ^{2}J(H$_{2'}$Rh) = 2.0)	C$_2$	50.4 (dd, ^{2}J(CP) = 21.4, 11.4)
	H$_2$	2.01 (m, ^{2}J(H$_2$H$_{2'}$) = 2.0, ^{2}J(H$_2$Rh) = 2.0	C$_6$	24.1 (br s)
	H$_6$	1.46 (br s)		
8	H$_5$	6.08 (m, ^{3}J(H$_5$H$_4$) = 4.1, ^{4}J(H$_5$H$_3$) = 0.5, ^{3}J(H$_5$P) = 2)	C$_5$	107.7 (qt, ^{2}J(CP) = ^{1}J(CRh) = 2.2)
	H$_4$	5.49 (dd, ^{2}J(H$_4$Rh) = 1.2, ^{3}J(H$_4$H$_3$) = 10.6)	C$_4$	96.9 (m)
	H$_3$	3.91 (t, ^{3}J(H$_3$H$_{2'}$) = 2.8, ^{3}J(H$_3$H$_2$) = 12.2)	C$_3$	78.6 (m)
	H$_{2'}$	2.05 (m, ^{2}J(H$_2$H$_{2'}$) = 13.7, ^{4}J(H$_2$P) = 3)	C$_6$	58.9 (q, J(CP or CRh) = 3.5)
	H$_2$	0.77 (t)	C$_2$	37.8 (m)
			C$_{Ph}$	146.3 (s), 130.1 (s), 128.5 (s), 127.1 (s)
9[g]	H$_3$	3.97 (q, ^{3}J(H$_3$H$_2$) = 6.0)	C$_3$	63.3 (m)
	H$_2$	−0.27 (qt, ^{4}J(H$_2$P) = 6.0)	C$_2$	14.8 (s)
10	H$_3$	4.00 (m, ^{3}J(H$_3$H$_2$) = 8.3, ^{3}J(H$_3$H$_{2'}$) = 9.3, ^{2}J(H$_3$Rh) = 1.5)	C$_3$	59.4 (br d, ^{2}J(CP) = 31.8)
	H$_{2'}$	3.1[c]	C$_2$	47.6 (br d, ^{2}J(CP) = 26.6)
	H$_2$	2.00 (m, ^{2}J(H$_2$H$_{2'}$) = 2.4, ^{2}J(H$_2$Rh) = 1.9)		
	H$_4$	2.00 (s)		
11	H$_3$	3.98 (m, ^{3}J(H$_3$H$_{2'}$) = 9.5, ^{2}J(H$_3$Rh) = 1.5)	C$_3$	60.0 (dd, ^{2}J(CP) = 25.0, 10.9)
	H$_{2'}$	2.71 (m, ^{2}J(H$_{2'}$H$_2$) = 2.6, ^{2}J(H$_{2'}$Rh) = 2.0)	C$_2$	48.5 (dd, ^{2}J(CP) = 22.8, 10.8)
	H$_2$	2.13 (m, ^{3}J(H$_2$H$_3$) = 8.1, ^{2}J(H$_2$Rh) = 1.7)	C$_4$	27.0 (br s)
	H$_4$	1.80 (br s, ^{3}J(H$_4$Rh) = 1.1)		

Table 2 (Continued)

| | ^{1}H NMR | | ^{13}C$\{^1$H$\}$ NMR | |
complex	assign	δ (multiplicity, $J)^{b,c}$	assign	δ (multiplicity, $J)^b$
	H$_{2'}$	5.15 (t, ^2J(H$_{2'}$H$_2$) = 13.8, ^3J(H$_{2'}$H$_3$) = 12.2)	C$_4$	58.5 (dd, J(CP or CRh) = 10.7, 4.2)
	H$_3$	3.63 (m, ^3J(H$_3$H$_2$) = 3.0)	C$_3$	55.0 (dt, J(CP or CRh) = 61.0, 10.9)
	H$_2$	2.8^e	C$_2$	39.0 (d, J(CP or CRh) = 3.7)
			C$_{Ph}$	147.2 (s), 129.9 (s), 128.3 (s), 126.3 (s)

^{a} All spectra were recorded at room temperature in CD$_2$Cl$_2$ solutions at 200.13 (^{1}H NMR) and 50.32 MHz (^{13}C$\{^1$H$\}$ NMR) unless otherwise stated. ^{b} Chemical shifts are given in ppm and are relative to either residual ^{1}H resonance in the deuterated solvent (^{1}H NMR) or the deuterated solvent resonance (^{13}C$\{^1$H$\}$ NMR). Key: s, singlet; d, doublet; t, triplet; q, quartet; qt, quintet; m, multiplet; br, broad. Coupling constants (J) are in hertz. ^{c} The J(HH) values were determined on the basis of ^{1}H$\{^{31}$P$\}$ NMR experiments. ^{d} Masked by the phenyl carbons of the BPh$_4^-$ anion and/or the triphos ligand. ^{e} Masked by the aliphatic protons of triphos. The chemical shift was determined from a ^{1}H$-^1$H 2D-COSY experiment. ^{f} Masked by the aromatic protons of the triphos ligand and of the BPh$_4^-$ anion. The chemical shift was determined from a ^{1}H$-^1$H 2D-COSY experiment. ^{g} The resonances due to the quaternary carbons bonded to rhodium could not be unambiguously assigned as they are masked by the phenyl carbons of the triphos ligand. ^{h} Quaternary carbons bonded to rhodium: δ 110.0 (d, J(CP or CRh) = 7.6 Hz), the other resonance could not be assigned.

and carbon resonances for all metal complexes and organo sulfur compounds as labeled in Tables 2 and 3.

Reactions of the Trihydride (triphos)RhH$_3$ with Thiophene and Benzo[b]thiophene. Stirring THF solutions of the trihydride (triphos)RhH$_3$[9] (**1**) with an excess of either thiophene (T) or benzo[b]thiophene (BT) at reflux temperature results in evolution of H$_2$ and formation of (triphos)Rh(η^3-SCH=CH—CH—CH$_2$) (**2**) and (triphos)Rh$\{\eta^3$-S(C$_6$H$_4$)CH=CH$_2\}$ (**3**), respectively. No reaction between **1** and T or BT occurs below 65 °C. Once formed, **2** and **3** are thermally stable in refluxing THF under nitrogen for several days.

Taking into account the effect of substituting rhodium for iridium (particularly, the low-field shift of the NMR resonances and the additional coupling constants to ^{103}Rh), all the spectroscopic data of the η^3-S,C,C-butadienethiolate **2** and of the η^3-S,C,C-2-vinylthiophenolate **3** are in excellent correlation with those of the analogous iridium derivatives (triphos)Ir(η^3-SCH=CH—CH=CH$_2$)[4] and (triphos)Ir$\{\eta^3$-S(C$_6$H$_4$)CH=CH$_2\}$.[5] Thus, like the Ir analogs, **2** and **3** are assigned octahedral structures in which the phosphorus atoms of triphos occupy three *fac* positions in the coordination polyhedron. The coordination about rhodium is completed by unsaturated thiolate ligands which use the sulfur atoms and the two carbon atoms of the distal olefinic ends. The latter moieties form quite robust bonds to the metal center [^2J(CP$_{trans}$) $\cong$ 33 Hz, ^2J(CP$_{cis}$) $\cong$ 9 Hz, ^1J(CRh) $\cong$ 9 Hz] as occurs in metal$-\pi$-olefin bonds exhibiting metallacyclopropane structure.[25]

No intermediate Rh species was observed to traverse the conversion of **1** to either **2** or **3** when the progress of the reactions was followed by ^{31}P$\{^1$H$\}$ and 1H NMR spectroscopies at a constant temperature of 65 °C. From this study it is also concluded that both compounds are stereochemically rigid on the NMR time scale in the temperature range from +65 to −90 °C.

Reactions of the Butadienethiolate Complex 2 with Electrophiles. Low-Temperature Reaction with HBF$_4$. Compound **2** in acetone at −20 °C reacts with HBF$_4$·OEt$_2$ to give, after addition of NaBPh$_4$, orange crystals of the η^4-C,C,C,S-thiocrotonaldehyde complex *anti*-[(triphos)Rh$\{\eta^4$-SCHCHCH(CH$_3$)$\}$]BPh$_4$ (**4**). The reaction is regio- and stereoselective: the proton is delivered to C$_2$, which consequently becomes a

methyl carbon (δH$_2$, 1.93; δC$_2$, 15.1), this methyl group being *trans* to H$_4$ [J(H$_3$H$_4$) = 8.0 Hz]. The thioaldehyde group is tetrahapto-bonded to the metal center in butadienoid fashion (*vide infra*) as indicated also by a variable-temperature NMR study. In fact, the fluxionality exhibited in solution by **4** involves only the phosphorus ligands (A$_3$X pattern at 20 °C, AMQX pattern with discernible J(PP) and J(PRh) at −40 °C) and not the CH$_3$CH=CH—C(H)=S ligand, which shows temperature-invariant chemical shifts of its carbon and hydrogen atoms. This situation is typical for d^8 MP$_3$(diene) complexes, particularly in the case of monosubstituted dienes.[5,26] It is generally agreed that no motion other than rotation of the diene can make the three phosphorus atoms equivalent in the fast exchange regime.[27] The thiocrotonaldehyde ligand changes its hapticity from η^4-C,C,C,S to η^2-C,S by reaction of **4** in CH$_2$Cl$_2$ with CO at room temperature. As a consequence of coordination of one CO molecule, the resulting complex [(triphos)Rh(CO)$\{\eta^2$-S=CH—CH=CH(CH$_3$)$\}$]BPh$_4$ (**5**) becomes stereochemically rigid on the NMR time scale (temperature-invariant ^{31}P AMQX spin system). The η^2-C,S bonding mode of the thioaldehyde is consistent with the low-field shift of the C$_3$ resonance (from 63.6 ppm in **4** to 125.6 ppm in **5**), the high-field shift of C$_5$ (from 112.1 ppm in **4** to 72.2 ppm in **5**), and the larger values of J(C$_5$Rh) and J(C$_5$P). In line with the structure of **5** reported in Table 2, the carbon and hydrogen atoms of the olefinic end C$_4$H$_4$=C$_3$H$_3$ lose or significantly reduce their coupling to the P and Rh nuclei. In contrast, J(H$_4$H$_5$) increases from 4.5 Hz in **4** to 11.5 Hz in **5**, which suggests a *trans* arrangement of H$_4$ and H$_5$. It is therefore reasonable to conclude that, after unfastening promoted by CO addition, the C$_4$−C$_3$ double bond rotates about the C$_4$−C$_5$ axis to give the more stable *s-trans* structure of the thioaldehyde (*vide infra*). A similar mechanism has previously been proposed for the racemization of dienetetrahaptoiron tricarbonyls.[28]

Thermal Isomerization of *anti*-[(triphos)Rh$\{\eta^4$-SCHCHCH(CH$_3$)$\}$]BPh$_4$ to *syn*-[(triphos)Rh$\{\eta^4$-SCHCHCH(CH$_3$)$\}$]-BPh$_4$. Complex **4** is rather unstable in solution above 10 °C. In THF at 20 °C, ca. 10% conversion to its red isomer *syn*-[(triphos)Rh$\{\eta^4$-SCHCHCH(CH$_3$)$\}$]BPh$_4$ (**6**) occurs in 24 h. At
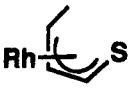
(25) (a) Barbaro, P.; Bianchini, C.; Meli, A.; Peruzzini, M.; Vacca, A.; Vizza, F. *Organometallics* **1991**, *10*, 2227. (b) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Albinati, A. *Organometallics* **1990**, *9*, 2283. (c) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P.; Ramirez, J. A. *Organometallics* **1990**, *9*, 226.
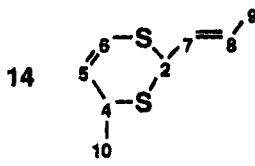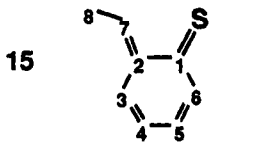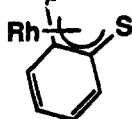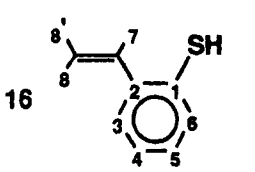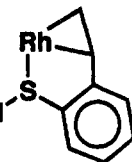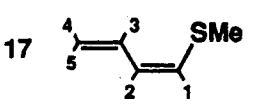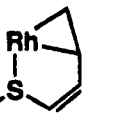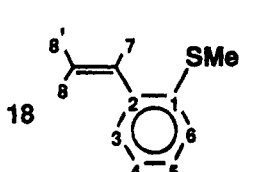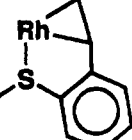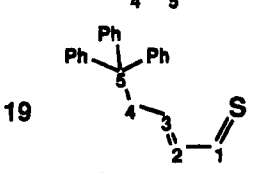
(26) Bianchini, C.; Caulton, K. G.; Johnson, T. J.; Meli, A.; Peruzzini, M.; Vizza, F. *Organometallics* **1995**, *14*, 933.

(27) Chardon, C.; Eisenstein, O.; Johnson, T.; Caulton, K. G. *New J. Chem.* **1992**, *16*, 781 and references therein.

(28) (a) Whitlock, H. W., Jr.; Markezich, R. L. *J. Am. Chem. Soc.* **1971**, *93*, 5290. (b) Whitlock, H. W., Jr.; Reich, C.; Woessner, W. D. *J. Am. Chem. Soc.* **1971**, *93*, 2483.

Table 3. Carbonylation Reactions (THF, 3 h)

complex	CO pressure (atm)	temperature (°C)	product
4	1	20	14
6	5	70	
9	1	20	15
10	5	20	16
7	5	40	17
11	5	40	18
8	5	70	19
12	5	70	20

reflux temperature, the transformation of **4** to **6** is quite rapid (3 h). Alternatively, the thermodynamically more stable *syn* isomer can straightforwardly be prepared by treatment of **2** in refluxing THF with a stoichiometric amount of HBF$_4$·OEt$_2$, followed by metathetical reaction with NaBPh$_4$. Compound **6** is thermally stable in refluxing THF.

The *trans* arrangement of H$_3$ and H$_4$ in the distal olefinic end C$_4$H$_4$=C$_3$H$_3$Me in **6** is supported by the *J*(HH) value of 10.3 Hz. All the other NMR parameters of **6** are in excellent correlation with those of the *anti* isomer **4**.

Interestingly, *anti* to *syn* isomerizations are well-known for transition metal complexes with substituted dienes for which the minor steric crowding of the *syn* isomer is believed to be the driving force of isomerization.[29]

Reaction with MeI. Treatment of **2** in THF at room temperature with a slight excess of MeI, followed by addition of NaBPh$_4$, gives complete transformation to [(triphos)Rh(η^3-MeSCH=CH—CH=CH$_2$)]BPh$_4$ (**7**) by selective delivery of

Me$^+$ to the sulfur atom. Compound **7** has a close precedent in [(triphos)Ir(η^3-MeSCH=CH—CH=CH$_2$)]BPh$_4$ similarly obtained by reaction of the Ir butadienethiolate (triphos)Ir(η^3-SCH=CH—CH=CH$_2$) with Me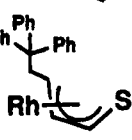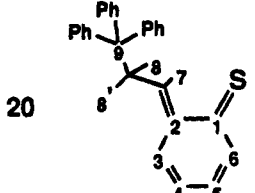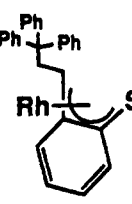I and authenticated by X-ray methods.[4] Since **7** and its iridium analog display fully comparable spectroscopic properties, the two compounds are assigned the same structure, *i.e.* the metal center is octahedrally coordinated by a *fac* triphos ligand and by a methyl buta-1,3-dienyl thioether which uses the sulfur atom and the two carbon atoms of the distal olefinic moiety.

Reaction with Ph$_3$CPF$_6$. Addition of a stoichiometric amount of triphenylcarbenium hexafluorophosphate to a CH$_2$-Cl$_2$ solution of **2** at room temperature yields red crystals of [(triphos)Rh{η^4-SCHCHCH(CH$_2$CPh$_3$)}]PF$_6$ (**8**), in which a 5,5,5-triphenyl-*trans*-2-pentenethial molecule binds rhodium *via* the four atoms of the α,β-unsaturated thioaldehyde moiety.

The structure of **8** has been determined by an X-ray analysis after the compound was recrystallized from CH$_2$Cl$_2$/ethanol to give **8**·CH$_2$Cl$_2$·0.5EtOH. This salt contains noninteracting BPh$_4$$^-$ and [(triphos)Rh{η^4-SCHCHCH(CH$_2$CPh$_3$)}]$^+$ ions, with CH$_2$-Cl$_2$ and EtOH filling holes in the lattice. An ORTEP drawing

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Synthesis of Unusual Organosulfur Compounds

J. Am. Chem. Soc., Vol. 117, No. 15, 1995 4341
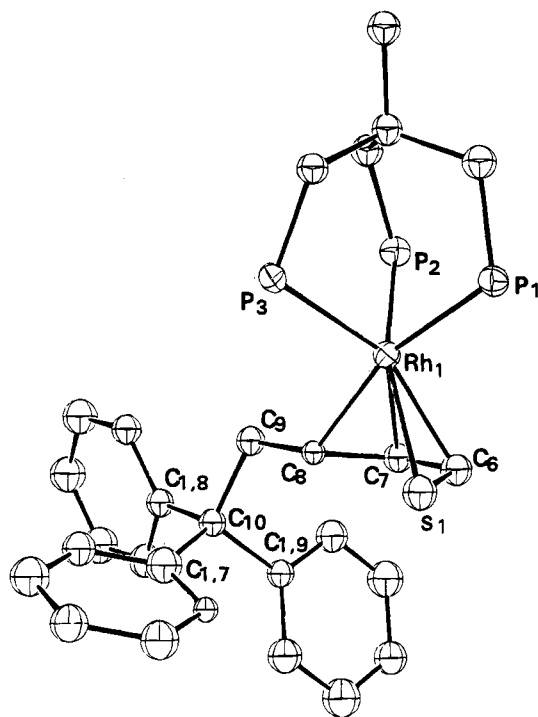
Figure 1. ORTEP drawing of the complex cation in 8·CH₂Cl₂·0.5EtOH. All of the hydrogen atoms and phenyl rings of triphos are omitted for clarity.

Table 4. Summary of Crystal Data for 8·CH₂Cl₂·0.5EtOH

formula	$C_{66}H_{64}Cl_2F_6O_{0.5}P_4Rh_1S_1$
formula weight	1309.01
crystal size, mm	0.37 × 0.40 × 0.12
crystal system	orthorhombic
space group	$P2_12_12_1$ (no. 19)
a, Å	10.834(6)
b, Å	15.012(6)
c, Å	39.902(9)
V, Å³	6489.66
Z	4
d_{calcd}, g cm⁻³	1.34
μ(Cu Kα), cm⁻¹	46.59
radiation	graphite-monochromated Cu Kα, λ = 1.5418 Å
scan type	$\omega - 2\theta$
2θ range, deg	5−120
scan width, deg	1.2 + 0.34 (tan θ)
scan speed, deg s⁻¹	0.03−0.06
total no. of data	4604
no. of unique data, $I > 3\sigma(I)$	1879
no. of parameters	297
R	0.079
R_w	0.082

of the complex cation is shown in Figure 1, and a list of selected bond distances and angles is presented in Table 5. While the P−Rh−P angles are equal and close to 90 °C (89.3(3)°ₐᵥ), the Rh−P3 bond length (2.354(8) Å) is longer than the other two distances (2.298(6) and 2.282(8) Å). This is consistent with a distorted square-pyramidal structure with one of the Rh−P bonds as the apical group. The other two basal positions are occupied by the C6−S1 and C7−C8 bonds, the C9 atom bearing a trityl substituent as a result of electrophilic attack by Ph₃CPF₆. The C7−C8 and C6−C7 separations are equal within experimental error (1.39(4) Å) and intermediate between single and double C−C bonds. The high standard deviation affecting the C6−S1 bond length (1.72(3) Å) prevents any comparison with analogous separations in η^2-C,S-thioaldehyde metal complexes (1.74−1.78 Å).[30] The bonding pattern from Rh to the pente-

Table 5. Selected Bond Distances (Å) and Angles (deg) for 8·CH₂Cl₂·0.5EtOH

Rh1−P1	2.298(6)	C7−C8	1.39(4)
Rh1−P2	2.282(8)	C8−C9	1.51(3)
Rh1−P3	2.354(8)	C9−C10	1.61(3)
Rh1−C6	2.12(3)	C6−S1	1.72(3)
Rh1−C7	2.24(3)	C10−C1,7	1.49(3)
Rh1−C8	2.30(2)	C10−C1,8	1.55(3)
Rh1−S1	2.42(7)	C10−C1,9	1.53(3)
C6−C7	1.39(4)		
P1−Rh1−P2	87.2(3)	Rh1−C7−C8	75(2)
P1−Rh1−P3	90.8(3)	Rh1−C7−C6	67(2)
P2−Rh1−P3	89.8(3)	Rh1−C8−C7	70(1)
P1−Rh1−C6	100.1(8)	Rh1−C8−C9	133(2)
P1−Rh1−C7	132.1(8)	S1−C6−C7	119(2)
P1−Rh1−C8	165.3(6)	C6−C7−C8	119(3)
P1−Rh1−S1	91.4(2)	C7−C8−C9	123(2)
P2−Rh1−C6	116.2(9)	C8−C9−C10	112(2)
P2−Rh1−C7	95.5(8)	C8−Rh−C7	35.5(9)
P2−Rh1−C8	100.7(6)	C8−Rh−C6	65(1)
P2−Rh1−S1	159.2(3)	C8−Rh−S1	76.8(6)
P3−Rh1−C6	152.1(9)	C7−Rh−C6	37(1)
P3−Rh1−C7	137.0(8)	C7−Rh−S1	70.4(8)
P3−Rh1−C8	101.5(6)	C6−Rh−S1	43.7(8)
P3−Rh1−S1	111.0(3)	C9−C10−C1,7	108(2)
Rh1−C6−S1	77(1)	C9−C10−C1,8	108(2)
Rh1−S1−C6	59(1)	C1,7−C10−C1,8	110(2)
Rh1−C6−C7	76(2)	C9−C10−C1,9	108(2)
		C1,7−C10−C1,9	117(2)
		C1,8−C10−C1,9	107(2)

Table 6. Extended Hückel Parameters ($1 + \kappa$ = 2.0, δ = 0.35)

atom	orbital	H_{ii} (eV)	ζ
H	1 s	−13.60	1.30
C	2s	−21.40	1.6250
	2p	−11.40	1.6250
S	3s	−20.0	1.8170
	3p	−13.30	1.8170
P	3s	−18.60	1.60
	3p	−14.0	1.60
Rh	5s	−8.09	2.1350
	5p	−4.57	2.100
	4d	−12.50	4.29 (0.5807)
			1.97 (0.5685)
Ir	6s	−11.36	2.50
	6p	−4.50	2.20
	5d	−12.10	5.80 (0.6698)
			2.56 (0.5860)

nethial ligand (Rh−C6, 2.12(3); Rh−C7, 2.24(3); Rh−C8, 2.30-(2); Rh−S1, 2.42(7) Å) is consistent with a stronger bonding interaction with the C−S moiety rather than with the distal olefinic end C7−C8, which shows an *E* structure. The C9, C8, C7, and C6 atoms are virtually coplanar (dihedral angle 179-(2)°), while the sulfur atom is slightly bent outside this plane (the dihedral angle S1−C6−C7−C8 is 10(3)°).

The bonding mode of the α,β-unsaturated thioaldehyde molecule in **8** is quite comparable to that of thioacrolein in Fe-(CO)₂(PPh₃)(η^4-C₃H₄S) prepared by reaction of Fe₂(CO)₄ with thiete.[30d,e]

In the field of metal-assisted transformations of thiophenes, the only compound that exhibits close structural analogies with **8** is the 3-propene-1-thiolate complex Cp*Rh(MeCOC₃Me₃S)

(30) (a) Park, J. W.; Henling, L. M.; Schaefer, W. P.; Grubbs, R. H. *Organometallics* **1990**, *9*, 1650. (b) Buhro, W. E.; Etter, M. C.; Georgiou, S.; Gladysz, J. A.; McCormick, F. B. *Organometallics* **1987**, *6*, 1150. (c) Buchwald, S. L.; Nielsen, R. B.; Dewan, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 1590. (d) Harlow, R. L.; Pfluger, C. E. *Acta Crystallogr., Sect. B* **1973**, *29*, 2633. (e) Dittmer, D. C.; Takahashi, K.; Iwanami, M.; Tsai, A. I.; Chang, P. L.; Blidner, B. B.; Stamos, I. K. *J. Am. Chem. Soc.* **1976**, *98*, 2795.

recently prepared by Rauchfuss *via* hydrolytic cleavage with aqueous KOH of coordinated tetramethylthiophene.[31]

Compound **8** is slightly fluxional in solution on the NMR time scale. At room temperature, the ^{31}P{^{1}H} NMR spectrum consists of three broad humps with no discernible *J*(PP) or *J*(PRh) coupling constants. The spectrum is fully resolved at −20 °C to give a canonical AMQX pattern. The hydrogen and carbon chemical shifts as well as the *J*(HH) coupling constants within the butadienoid system $C_3H_3=C_4H_4-C_5(H_5)=S$ in **8** are almost identical with the corresponding values in **6**, thus confirming the proposed *syn* structure of the latter complex.

Reactions of the 2-Vinylthiophenolate Complex 3 with Electrophiles. Low-Temperature Reaction with HBF₄. Like the butadienethiolate analog, compound **3** reacts in THF with HBF₄·OEt₂ at −20 °C to give a product in which a proton is added to C_2. In the resulting violet complex, [(triphos)Rh{η^4-S(C₆H₄)CH(CH₃)}]BPh₄ (**9**), the metal center is coordinated by a 2-ethylidenecyclohexadienethione ligand *via* the ethylidene double bond and the C=S bond.[5] The square-pyramidal geometry of the complex cation is completed by a *fac* triphos ligand. While the regioselective delivery of the proton to C_2 is unequivocally shown by the appearance of a methyl resonance in the ^{1}H and ^{13}C{^{1}H} spectra (δH₂ −0.27, quartet; δC₂ 14.8, singlet), the NMR data do not discriminate between *anti* and *syn* structures of **9**. The thermal behavior of the latter complex in solution is not of help for discriminating between the two structures. In fact, heating a THF solution of **9** above room temperature does not result in a different orientation of the methyl as occurs in the case of **4**, but instead, an intramolecular hydrogen shift from carbon to sulfur occurs (see below). In conclusion, no precise stereochemistry can be assigned to the ethylidene moiety in **9** (see Scheme 3) even though the reaction conditions suggest the *anti* conformation.

Thermal Isomerization of 2-Ethylidenecyclohexadienethione in 9 to 2-Vinylthiophenol in 10. Compound **9** is rather stable in room-temperature solutions. On long standing, however, the violet complex converts into the yellow green isomer [(triphos)Rh{η^3-HS(C₆H₄)CH=CH₂}]BPh₄ (**10**). A complete conversion occurs in several days and is greatly accelerated by an increase of the temperature to 80 °C which represents the best compromise between a reasonable reaction rate (18 h for 300 mg) and the lack of appreciable decomposition.

Upon thermolysis, a hydrogen atom moves intramolecularly from the methyl group of **9** to its thiolate sulfur to give a 2-vinylthiophenol ligand. The most evident ^{1}H and ^{13}C NMR spectroscopic consequence of this proton transfer is the disappearance of any methyl resonance in the spectra of **10** with the exception of the one pertaining to the triphos ligand. Moreover, the chemical shifts of the hydrogen and carbon atoms of the newly generated olefinic end $C_2H_2(H_{2'})=C_3H_3-$ go back to the values of the neutral 2-vinylthiophenolate precursor (a slight high-field shift of the phosphorus resonances may be attributed to the cationic nature of **10**). Finally, the ^{1}H NMR spectrum of **10** in CD_2Cl_2 contains a new resonance, a singlet, at 2.0 ppm which disappears by addition of a drop of D_2O in the NMR tube. Both the position of this signal and the fast exchange of the parent hydrogen with deuterium from D_2O are consistent with the presence in **10** of an SH group. This is also supported by the experimental observation that **10** in THF is deprotonated to **3** by *t*-BuOK as well as by the reaction with CO (*vide infra*).

Reactions with MeI and Ph₃CPF₆. The 2-vinylthiophenolate complex **3** reacts with either MeI or Ph₃CPF₆ in a manner

essentially identical with that of the butadienethiolate congener **2**. The methyl group is selectively added to the sulfur atom, and the addition does not appreciably alter the NMR parameters of the vinyl moiety of the starting thiophenolate ligand (δH₂, 2.71; δH₂', 2.13; δH₃, 3.98; δC₂, 48.5; δC₃, 60.0). In the stereochemically rigid product [(triphos)Rh{η^3-MeS(C₆H₄)-CH=CH₂}]BPh₄ (**11**), the *o*-(methylthio)styrene ligand is, in fact, still η^3-anchored to rhodium *via* the C_2-C_3 double bond and the sulfur atom. The NMR parameters of **11** are in good correlation with those of the known iridium analog [(triphos)-Ir{η^3-MeS(C₆H₄)CH=CH₂}]BPh₄[5] and, most importantly, with those of **10** as expected for compounds differing only in the substituent at the sulfur atom (H in **10**, CH₃ in **11**).

Extensive modification of the structure and bonding mode of the thio ligand framework, however, occurs in the product of the reaction between **3** and the trityl cation. The addition of the latter group to C_3 converts the vinylthiophenolate ligand into 2-(3,3,3-triphenylpropylidene)cyclohexadienethione which uses its heterodiene moiety to coordinate the metal center. Indeed, the resulting complex [(triphos)Rh{η^4-S(C₆H₄)CH(CH₂-CPh₃)}]PF₆ (**12**) exhibits ^{1}H and ^{13}C NMR parameters which correlate with those of the analogous groups of atoms in either the 5,5,5-triphenyl-*trans*-2-pentenethial complex **8** (δC₂, 39.0; δC₄, 58.5) or the 2-ethylidenecyclohexadienethione derivative **9** (δC₃, 55.0; δH₃, 3.63; ^{3}*J*(H₃H₂) = 3.0 Hz).

Carbonylation Reactions. All the rhodium complexes obtained by addition of electrophiles to either the butadienethiolate **2** or the vinylthiophenolate **3** were dissolved in THF and then subjected to a CO atmosphere in autoclaves. In the ranges of temperature from 20 to 70 °C and of CO pressure from 1 to 5 atm, all complexes quantitatively transform into the known dicarbonyl [(triphos)Rh(CO)₂]Y[9] (Y = BPh₄, PF₆) within 3 h, while the neutral thio ligands are liberated in solution in quantitative yield.

Table 3 summarizes the reaction conditions and the structures of the organosulfur compounds that have been purified by TLC and then characterized in CDCl₃ solution. With the exception of thiocrotonaldehyde, all products are stable as single molecules in solution. Thiocrotonaldehyde which is displaced from either **4** or **6**, spontaneously dimerizes to 2-*n*-propenyl-4-methyl-4*H*-1,3-dithiine (**14**) *via* a Diels−Alder-type condensation. Another organosulfur compound, probably the 3-*n*-propenyl-4-methyl-4*H*-1,2-dithiine isomer, was also formed but in a trace amount that prevented an accurate characterization. Identification of the 1,3-dithiine **14** was made by means of ^{1}H and ^{13}C{^{1}H} NMR spectroscopies corroborated by a comparison with the spectral data of the known 2-vinyl-1,3-dithiine similarly generated by Diels−Alder dimerization of thioacrolein.[13] Consistent with its major thermodynamic stability, the *syn* isomer **6** is carbonylated at a higher temperature (70 °C) than is required for the *anti* isomer **4** (20 °C).

Because of the presence of the bulky trityl substituent, 5,5,5-triphenyl-*trans*-2-pentenethial (**19**) liberated in the course of the carbonylation reaction of **8** exists as a monomeric species, which represents a new, rare example of a stable α,β-unsaturated thioaldehyde.[32] The *E* structure of **19** is suggested by the *J*(H₃H₂) and *J*(H₂H₁) values of 15.6 and 7.8 Hz, respectively.

2-Vinylthiophenol (**16**),[14] *cis*-1-(methylthio)butadiene[15] (**17**), and *o*-(methylthio)styrene[16] (**18**) obtained from **10**, **7**, and **11**, respectively, have been identified by comparing their ^{1}H and ^{13}C{^{1}H} NMR and MS spectra with those reported in the literature for authentic specimens.

New molecules are the 2-ylidenecyclohexadienethiones **15** and **20** differing in the substitution of the terminal ylidene. While

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Scheme 4
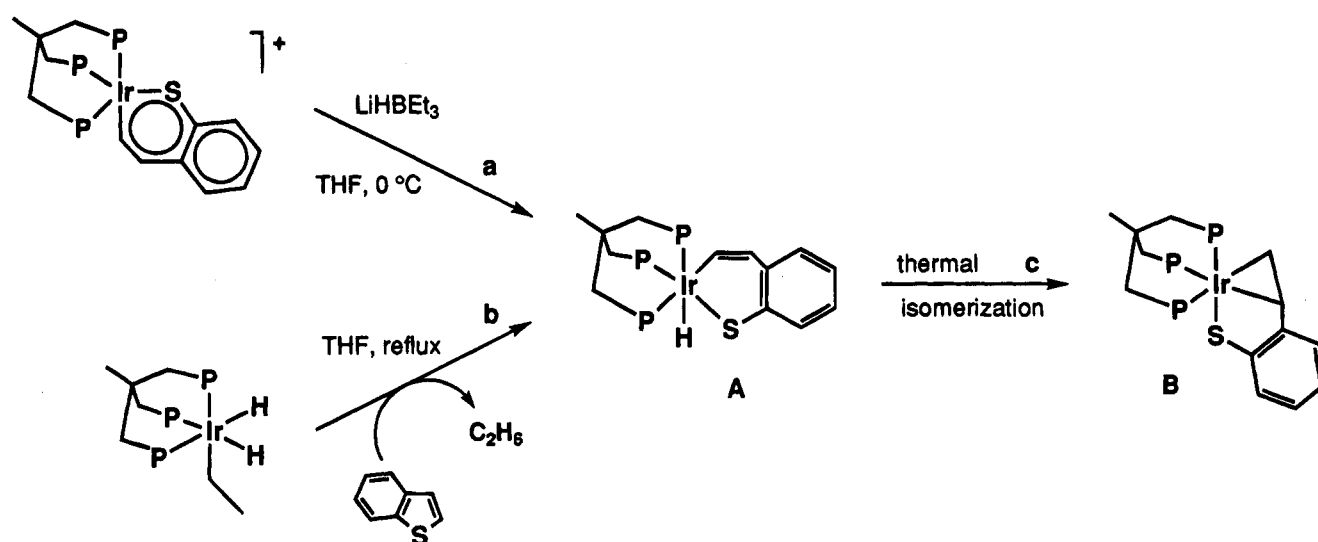
nicely characterizable by NMR spectroscopy, the mass spectra of **20** (EI or FAB) were poorly informative because the inherent stability of the triphenylcarbenium fragment precludes detection of the molecular ion peak. Unambiguous identification of both compounds was provided by NMR spectroscopy; in particular, the positions of C_1 (207.4 ppm in **15**; 206.8 ppm in **20**) and of C_7 (124.1 ppm in **15**; 147.5 ppm in **20**) in the $^{13}C\{^1H\}$ NMR spectrum rule out the alternative structure with a bond between the S and C_7 atoms.

Discussion

Opening and Reduction of Thiophene and Benzo[*b*]-thiophene by the [(triphos)RhH] Fragment. Thermolysis of the trihydride **1** in THF is a well-known procedure to generate the 16-electron fragment [(triphos)RhH].[9,25b,c] Like all 16-electron systems that cannot exist in the square-planar geometry, [(triphos)RhH] is highly energetic and thus an excellent candidate for the oxidative cleavage of chemical bonds due to its capability of lowering the energy barrier to insertion.[33,34] Carbon—sulfur bonds from T or BT are evidently broken by the [(triphos)RhH] fragment. The observation of no intermediate in the conversion of **1** into either **2** or **3** indicates that the energy of activation required to promote the reductive elimination of H_2 from **1** is higher than those necessary to accomplish both insertion of rhodium into a C—S bond from either T or BT and migration of hydride to the α-carbon of the resulting metallathiacycle. Fortunately, valuable mechanistic information on these transformations is provided by prior[4,5] and current work from this laboratory with a kinetically inert third-row metal such as iridium. Scheme 4 summarizes the results obtained for BT, but quite analogous results have been observed for T (path a).[4] Path b is more pertinent to the piece of chemistry described in this paper. Upon thermolysis of (triphos)Ir(H)₂(C_2H_5) in the presence of BT, the [(triphos)IrH] fragment inserts into a C—S bond to give the iridathiacycle hydride (triphos)Ir(H)(η^2-C,S-C_8H_6S) (**A**) and then, as the reaction proceeds, uniquely the 2-vinylthiophenolate (triphos)Ir{η^3-S(C_6H_4)CH=CH₂} (**B**) (step c).[35] The latter compound is the thermodynamic product of the

reaction as shown by the independent synthesis of B from route a,c.[5] In view of this evidence, it is concluded that also **2** and **3** are most likely formed *via* insertion of the [(triphos)RhH] fragment into a C—S bond of BT, followed by selective delivery of hydride from the metal to the vinyl α-carbon atom.

A variety of transition metal fragments have been reported by Jones,[36] Angelici,[37] Rauchfuss,[6,38] Field,[39] Merola,[40] and Maitlis[41] to cleave C—S from thiophenic molecules yielding metallathiacycles. Among mononuclear systems, the present rhodium fragment is unique in that it bears a hydride ligand which serves to initiate the reduction of the cleaved thiophenic molecules.

The importance of using metal hydrido complexes for the activation of thiophenic molecules is further demonstrated by a recent work from Jones and co-workers, who reported on the hydrodesulfurization of T to butadiene and butane assisted by the dimer [(C_5Me_5)IrH₃]₂.[42] On the other hand, it is worth mentioning that transformation of T to butadienethiolate has also been achieved by external addition of either H⁻ to [CpRu(η^5-T)]$^{+7}$ or H⁺ to (C_6Me_6)Ru(η^4-T).[43] Transformation of T to a reduced butanethiolate ligand has also been reported.[44]

A question of much current interest regards the anchoring mode of the thiophenic molecule to the metal center prior to C—S scission. There is general consensus on two effective bonding modes: η^1-*S*-coordination and η^2-*C,C'*-coordination.[2] Both bonding modes seem to be simultaneously operative when the activating metal fragment bears 14 electrons as in the case of the [(triphos)Ir]⁺ system which anchors BT in η^3-*C,C',S*-fashion prior to C—S bond scission.[5]

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Due to the lack of detectable intermediates along the transformation of **1** into either **2** or **3**, nothing can be said about the initial interaction of the thiophenic molecules with the [(triphos)-RhH] fragment. We may only report that [(triphos)RhH] and the isoelectronic system [(triphos)RhCl] are appropriately designed for binding both C=S and C=C bonds in dihapto fashion, see for example (triphos)RhH(η^2-C$_2$H$_4$),[25c] (triphos)-RhCl(η^2-CS$_2$),[45] and (triphos)RhCl(η^2-C$_2$H$_4$).[25c]

Reactions of the Butadienethiolate and Vinylthiophenolate Rh Complexes with Electrophiles. The reactions of the butadienethiolate **2** and of the 2-vinylthiophenolate **3** with electrophiles apparently show that each compound contains two nucleophilic sites on the T- or BT-derived ligands. These sites are the sulfur atom and the C$_2$ carbon atom of the distal olefinic moiety. This finding and the fact that the two nucleophilic centers are capable of discriminating among the various electrophiles investigated excite practical and fundamental interest. Fundamental motivations arise from the observation that electrophiles are not apparently discriminated on the basis of their size (the two extremes H$^+$ and Ph$_3$C$^+$ show preference for the carbon atom). From the practical perspectives, this chemistry is rich of implications for gaining further insight into the HDS of thiophenic molecules at the molecular level (see the following section).

One could also conceive the reactions with Ph$_3$C$^+$ following a radical mechanism[46] instead of a direct electrophilic attack,[47] since the starting neutral species **2** and **3** are oxidized in CH$_2$-Cl$_2$ (in the cyclic voltammetry time scale) to their monocationic derivatives at potentials of −0.07 V (E_p) and +0.05 V ($E^{o'}$), respectively, which are covered by the trityl cation (+0.27 V);[48] also, the cationic rhodium species [(triphos)Rh{η^3-S(C$_6$H$_4$)-CH=CH$_2$}]$^+$ is sufficiently long-lived ($t_{1/2} \cong$ 10 s) to react with a trityl radical in solution.[49]

In order to clarify this point, we have carried out some additional experiments: the reactions between **2** or **3** and Ph$_3$C$^+$ are substantially quenched by 5,5-dimethyl-1-pyrroline *N*-oxide, a well-known spin trap;[50] however, such reactions are not affected by the presence of oxygen, which is known to inhibit trityl radical reactions.[46a,48b] Furthermore, we have observed that the trityl cation reacts rapidly with 5,5-dimethyl-1-pyrroline *N*-oxide by non-radical processes, which explains the inhibition observed. Finally, the reactions between **2** or **3** and Ph$_3$C$^+$ were found not to be affected by the presence of the stable free radical TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy), while the trityl radical (generated electrochemically) does couple rapidly with

Table 7. Calculated Charges (q) on Thiametallacycle Cores of **2′**, **2″**, **3′**, and **3″**

	Rh		Ir	
	2′ (T)	**3′** (BT)	**2″** (T)	**3″** (BT)
q(M)	−0.76857	−1.12879	−1.14269	−1.55744
q(S)	−0.26501	−0.23669	−0.21758	−0.19126
q(C$_5$)	−0.03708	0.08248	−0.02922	0.08574
q(C$_4$)	−0.19469	0.01692	−0.18624	0.01832
q(C$_3$)	−0.25034	−0.28990	−0.17808	−0.23496
q(C$_2$)	−0.40631	−0.41273	−0.34508	−0.36427

TEMPO. We can therefore conclude that the attacks of the trityl cation on **2** or **3** are truly electrophilic and not radical in nature.

In order to shed some further light on the bifunctional character of **2** and **3**, a theoretical analysis has been carried out. Extended Hückel molecular orbital calculations have been performed for the model compounds (PMe$_3$)$_3$Rh{η^3-S—CH=CHCH=CH$_2$} (**2′**) and (PMe$_3$)$_3$Rh{η^3-S(C$_6$H$_4$)CH=CH$_2$} (**3′**), with a geometry for the metallacycle cores taken from the crystal structure of the closely related complex cation [(triphos)-Ir{η^3-S(Me)—CH=CHCH=CH$_2$}]$^+$.[4] The calculations were extended to the iridium analogs of **2′** and **3′** (**2″** and **3″**, respectively) for comparison purposes; atom numbering is the same as in Table 2.

The electronic structures of the four thiametallacycles studied display the typical features for the d^6 metal ion (Rh^{3+}, Ir^{3+}) in a pseudo-octahedral field formed by the three phosphorus donor atoms plus S, C$_2$, and C$_3$. The bonding of the organic fragment to [(PMe$_3$)$_3$M]$^{3+}$ (M = Rh, Ir) can be envisaged as a 6-electron donation from S, C$_2$, and C$_3$ to the metal-containing fragment. The reactivity of the resulting thiametallacycles may then be associated with the presence of a lone pair on the sulfur and with the geometrical parameters of the three-membered ring (Ir—C$_2$—C$_3$) and the five-membered ring (Ir—S—C$_5$—C$_4$—C$_3$).

The charges on the atoms of the thiametallacycles are shown in Table 7. These data clearly show that in all cases the ligand atom most susceptible to electrophilic attack is C$_2$. A detailed analysis of the electronic structure reveals that this is a consequence of the strain observed in the three-member ring, since the overlap between the orbital associated to the electron pair on C$_2$ and the metal orbital of adequate symmetry is small.

From these results it becomes evident that the charges on the thiametallacycles alone cannot unambiguously explain our experimental observations.

We can further argue that Ph$_3$C$^+$, being a worse electrophile than CH$_3$$^+$, attacks the better nucleophile, *i.e.* C$_2$; however, H$^+$ which is the best electrophile in this series also shows preference for the carbon atom, probably because the formation of a C−H bond is enthalpically favored over formation of an S−H bond. Only for the reaction of H$^+$ with the 2-vinylthiophenolate complex **3**, the C−H bond formation product **9** is thermodynamically less stable than the S−H bond formation product **10**. In this case, a substantial contribution to the major thermodynamic stability of the S−H bond formation product may be provided by the restoration of the aromaticity in the C$_6$ ring. In the case of CH$_3$$^+$, selective attack to the sulfur atom has been invariably observed *e.g.* for the analogous complex (triphos)-Ir{η^3-S—CH=CHCH=CH$_2$}[4] and for other related butadienethiolate derivatives.[7] We have recently observed that **2** and **3** react with RCOCl (R = *e.g.* Me, Ph); in both cases, attack by the acyl also occurs selectively at the sulfur; again, a carbon electrophile of medium size goes to the sulfur to produce a C−S bond.[35] The selective attack by Ph$_3$C$^+$ at the carbon atom may be thus driven by steric effects (repulsion between the phenyl rings of the ligand and of the trityl group).

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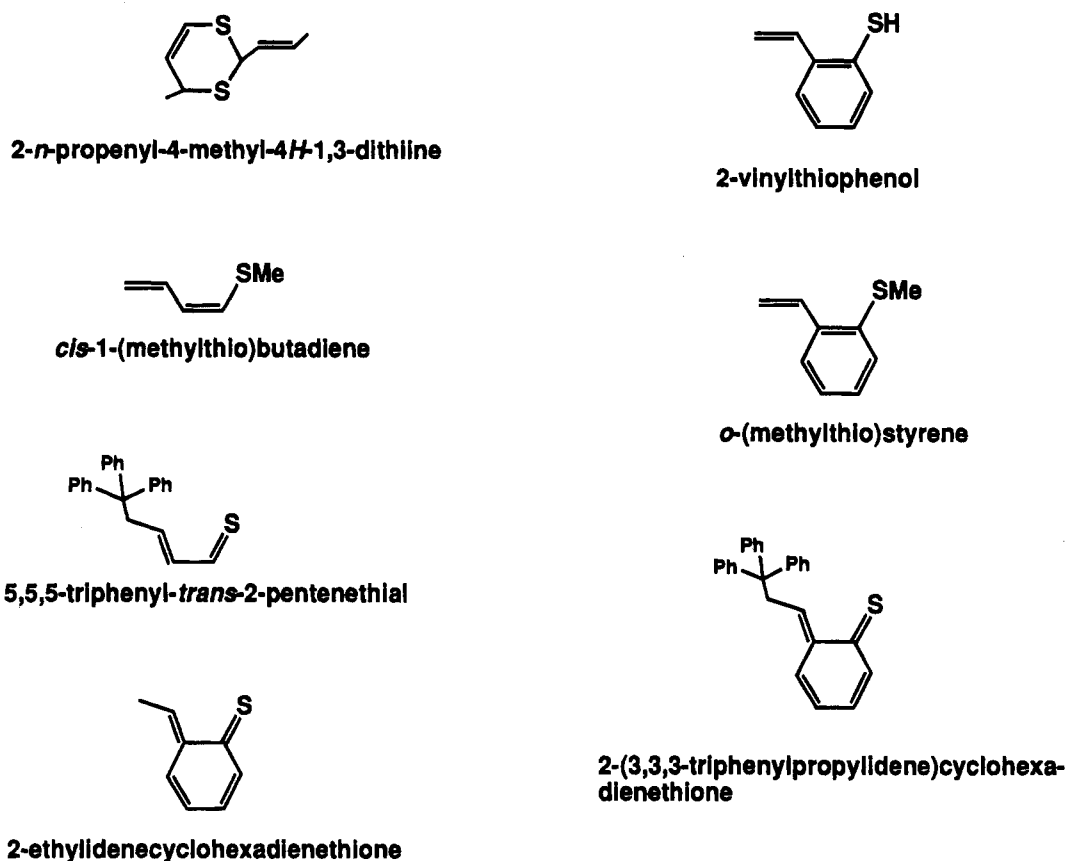
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(49) A detailed description of the electrochemistry of **2** and **3** will be the subject of a forthcoming paper.

(50) See the collection of papers in *Can. J. Chem.* **1982**, *60*, 1379.

Chart 1

2-*n*-propenyl-4-methyl-4*H*-1,3-dithiine

***cis*-1-(methylthio)butadiene**

5,5,5-triphenyl-*trans*-2-pentenethial

2-ethylidenecyclohexadienethione

2-vinylthiophenol

***o*-(methylthio)styrene**

2-(3,3,3-triphenylpropylidene)cyclohexa-dienethione

In conclusion, there seems to be a subtle balance between the nature of the electrophile (electronic and steric) and that of the nucleophile which determines the type of chemical bonds which are ultimately formed upon electrophilic attack to the thiametallacycles **2** and **3**.

Implications for HDS of Thiophenic Molecules. Homogeneous reactions of thiophenes with transition metals constitute a modeling approach for the elucidation of the HDS mechanism.[3] A great deal of work has already been developed in this sense, and a variety of activation modes of T and BT have been discovered, but little work has been carried out on the reactivities of open C_4H_4S and C_8H_6S fragments.[4-7] Therefore, some of the results presented in this paper may also contribute to gaining further insight into the HDS process.

An unambiguous point is that the vinyl moiety in metallated C_4H_4S and C_8H_6S systems may undergo reductive coupling with a hydride ligand.[4,5] Also, the resulting alkene acquires nucleophilic character and consequently becomes susceptible to attack by electrophiles, including H^+. Thus the α-CH group of metallated thiophenes can be converted into CH_3 *via* sequential addition of H^- and H^+. On the other hand, previous work from this laboratory has shown that molecular hydrogen can reduce the iridabenzothiabenzene complex [(triphos)Ir(η^2-*C,S*-C_8H_6S)]$^+$ to the 2-ethylbenzenethiolate complex (triphos)Ir(H)$_2${S(C$_6$H$_4$)-C$_2$H$_5$} through the intermediacy of [(triphos)Ir{η^4-S(C$_6$H$_4$)CH-(CH$_3$)}]$^+$, which is analogous to **9**.[5] It is not clear as yet whether this conversion proceeds *via* either heterolytic splitting or oxidative addition of H_2. However, the fact that the hydrogenation of both metallathiabenzene and metallabenzothiabenzene complexes may initially occur by sequential addition of H^- and H^+ strengthens the belief that heterolytic reaction mechanisms may be operative in hydrotreating catalysis.[3d,51]

Further evidence of the potential role of protons in activation paths of thiophenic molecules at metal centers is provided by

the thermal behavior of the 2-ethylidenecyclohexadienethione complex **9**, which is the kinetic product of the reaction between the 2-vinylthiophenolate complex **3** and H^+. Thermolysis of **9** in THF results in hydrogen transfer from the methyl of the ethylidene group to the sulfur atom to give the 2-vinylthiophenol complex **10**. As previously mentioned, it is very much likely that the driving force to this proton transfer is the proclivity of the electronically localized ethylidenecyclohexadienethione ligand to restore the aromaticity of the C_6 ring. As a matter of fact, the η^4-*C,C,C,S*-thiocrotonaldehyde derivative **6**, analogous to **9**, is thermally stable.

Thiophenes as Synthetically Useful Molecules for Unusual Organosulfur Compounds. Chart 1 summarizes the various unsaturated organosulfur compounds obtainable by T and BT activation at rhodium. Not all compounds are new. Some of them, *i.e. cis*-1-(methylthio)butadiene,[15] 2-vinylthiophenol,[14] and *o*-(methylthio)styrene,[16] have already been prepared by alternative procedures. These generally involve a large number of steps and thus exhibit low yields. The present procedures still involve several steps but offer the advantage of using cheap, harmless thiophenic molecules which can easily be functionalized. Thus, the present synthetic method may provide alternative access to variously substituted 1-(methylthio)butadienes, 2-vinylthiophenols, or *o*-(methylthio)styrenes. It is also worth mentioning that all rhodium is recovered at the end of the reactions.

New molecules are 2-*n*-propenyl-4-methyl-4*H*-1,3-dithiine and 5,5,5-triphenyl-*trans*-2-pentenethial. The former product is formed *via* dimerization of thiocrotonaldehyde. Such a dimerization is prevented by the bulky trityl substituent that allows the corresponding α,β-unsaturated thioaldehyde to exist

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as stable monomeric species. Indeed, the tendency with thioaldehydes is for spontaneous oligomerization[13,52] to occur unless there is electronic or steric stabilization.[32,53] This inherent instability represents a serious limit to the preparation of thioaldehydes, which are very useful compounds in organic synthesis, particularly for the incorporation of sulfur into the synthesis of heterocycles or natural products.[13b,54] This problem may be overcome by using thioaldehyde metal complexes which are known to react with dienes *via* Diels−Alder addition to give thioaldehyde−diene adducts.[55] From this point of view, the metal-assisted conversion of thiophenes to thioaldehydes (see complexes **4**, **5**, **6**, and **8**) provides a new, synthetically useful method for the preparation of heterocycles *via* Diels−Alder reactions with dienes. Current work from this laboratory is being developed in this direction.

To the best of our knowledge, unprecedented molecules are also 2-ethylidenecyclohexadienethione and 2-(3,3,3-triphenylpropylidene)cyclohexadienethione. Both molecules are electronically rich conjugated systems which may "open the door"

after further simple structural elaboration (*e.g.* Diels−Alder, nucleophilic substitution, oxidation of sulfur, and reduction) to a vast array of new organic or synthetically difficult molecules. Interesting structural features include the conjugated 8-π-electron (planar) system bearing an electronically unsymmetric thioketone terminal group and, in **12**, the bulky trityl substituent.

In conclusion, independent of its relevance for elucidation of the HDS mechanism, the organometallic chemistry of thiophenes constitutes a field of research with enormous potential in the synthesis of unusual organosulfur compounds.

Supplementary Material Available: Tables of positional and thermal parameters and anisotropic U values for **8**•CH_2-Cl_2•0.5EtOH (5 pages); listing of observed and calculated structure factors for **8**•CH_2Cl_2•0.5EtOH (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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