The Catalytic Transformation of Benzo[b]thiophene to 2-Ethylthiophenol by a Soluble Rhodium Complex: The Reaction Mechanism Involves Ring Opening Prior to Hydrogenation

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Abstract: The thermally generated 16-electron fragment [(triphos)RhH] reacts with benzo[*b*]thiophene (**BT**) by C−S bond scission to ultimately yield the 2-vinylthiophenolate complex (triphos)Rh[η^3-S(C_6H_4)CH=CH_2] (**1**), which is an efficient catalyst precursor for the hydrogenation of **BT** into 2-ethylthiophenol (**ETSH**) and, to a lesser extent, into 2,3-dihydrobenzo[*b*]thiophene (**DHBT**) at 160 °C and 30 atm H_2 [triphos = $MeC(CH_2PPh_2)_3$]. The mechanism of this unusual catalytic transformation has been established by high pressure NMR spectroscopic (HPNMR) studies combined with the isolation and characterization of key species related to the catalysis. Under catalytic conditions **1** was shown by HPNMR to be completely transformed into (triphos)$Rh(H)_2$[*o*-S(C_6H_4)C_2H_5] (**2**) and [(η^2-triphos)-Rh{μ-*o*-S(C_6H_4)C_2H_5}]$_2$ (**3**); removal of H_2 in the presence of **ETSH** leads to the quantitative formation of (triphos)-RhH[*o*-S(C_6H_4)C_2H_5]$_2$ (**4**), which is also the terminal state of the catalytic system in all experiments carried out in a high pressure reactor under various reaction conditions. The dimer **3** was prepared in a pure form by reaction of (triphos)RhH_3 with 1 equiv of **ETSH** in THF and reacted with excess **ETSH** to produce **4**, with H_2 to give **2**, and with CO to yield (triphos)RhH(CO)[*o*-S(C_6H_4)C_2H_5] (**6**). Conversely, **3** could be obtained by thermally induced reduction elimination of H_2 from **2** even under 30 atm of H_2 or of **ETSH** from **4**. The formation of the dihydride **2** from the vinylthiophenolate derivative **1** under H_2 (>15 atm) was also observed by HPNMR; this reaction was mimicked by the stepwise addition of H^+ to yield [(triphos)Rh{η^4-S(C_6H_4)CH(CH_3)}]BF_4 (**7**). Reaction of the latter complex with H^- produces (triphos)RhH[η^2-S(C_6H_4)CH(CH_3)] (**8**), which converts to the dimer **3** by reductive coupling of the terminal hydride ligand with the metalated alkyl substituent in the thioligand, via the unsaturated fragment [(triphos)Rh{*o*-S(C_6H_4)C_2H_5}]. In the mechanistic picture proposed, the catalytically active species for both reactions is [(triphos)RhH] generated from **2** by the rate-determining reductive elimination of **ETSH**. The hydrogenation of **BT** to **ETSH** occurs after the substrate has been C−S inserted, although hydrogenation to **DHBT** also takes place as a minor, parallel path. Then η^1-*S* and η^2-2,3-**BT** isomers probably exist in equilibrium, but the η^1-*S* intermediate prevails over the η^2-2,3 isomer for steric reasons, thus determining the chemoselectivity of the reaction. The chemistry herein described provides further insight into the mechanistic aspects of HDS reactions on solid catalysts.

Introduction

Sulfur in fossil fuel feedstocks is contained in a variety of organic compounds, such as thiols, disulfides, and the more refractory thiophenes, benzothiophenes, and dibenzothiophenes. The removal of sulfur from fossil materials is referred to as hydrodesulfurization (HDS) and has enormous technological importance for several reasons, among which is a substantial contribution to the decrease of acid rain upon fuel combustion.[2] Conventional HDS catalysts are prepared by coimpregnation of Mo (or W) salts on an alumina support, followed by sulfidation with H_2S/H_2. Increased reactivity is achieved by introduction of metal promoters such as Co, Ni, Ru, Rh, and Ir.

International regulations on emission control will soon require reducing the sulfur content in fuels and distillates to less than 300 ppm. Under this incentive, intense research efforts are currently being directed to the development of more efficient or alternative routes to improve gasoline quality by reducing the content of sulfur without making significant changes in octane rating. Major sources of aromatic sulfur compounds in gasoline are coking and cracking napthas. In the latter, the content of sulfur may be as high as 1300 ppm with a 2:1 predominance of benzo[*b*]thiophenes over thiophenes.[3] This characteristic of fuels such as these increases the difficulty of their purification, as benzothiophenes are more refractory to HDS than thiophenes,[4] and motivates the increasing interest in the chemistry of benzo[*b*]thiophene (**BT**).

The most widely accepted mechanisms proposed for HDS of **BT** over solid catalysts are shown in Scheme 1.[2c,5] Path **a** begins with the selective hydrogenation to dihydrobenzo[*b*]-thiophene (**DHBT**) prior to desulfurization, while path **b**

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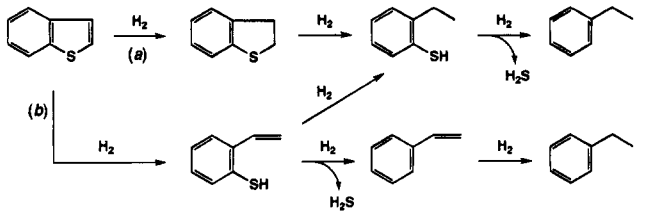
Scheme 1



involves initial C−S bond scission, followed by hydrogenation of the cleaved **BT** molecule.

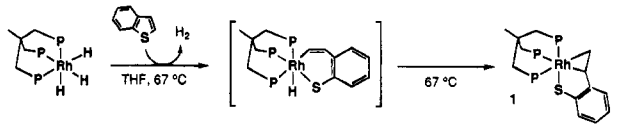
A great deal of fundamental research has been carried out in trying to understand the salient features of the HDS process of benzothiophenes. Insights into the mechanism have primarily been obtained from the study of the coordination and reactivity of **BT** with soluble metal complexes[6] as well as in surface science studies of **BT** on single crystals.[7] The various bonding modes of **BT** to metal centers,[8,9] and the stoichiometric reactions leading to C−S bond cleavage,[10] hydrogenation,[10a,e] and desulfurization[10e,f] have been described in detail. Some examples of regioselective hydrogenation of **BT** to **DHBT**, catalyzed in the homogeneous phase by Rh and Ru systems, have also been reported.[11,12]

Despite the numerous studies devoted to the homogeneous metal-assisted activation of **BT**, there are no reports which detail the catalytic opening and hydrogenation of **BT** assisted by transition metal complexes. Thus, most of the elementary steps involved in HDS of **BT** are still the result of indirect evidence.

In a previous report, we have shown that the 16-electron fragment [(triphos)RhH], generated *in situ* by thermolysis of (triphos)RhH_3 in THF, is active toward the oxidative addition of a C−S bond from **BT** [triphos = $MeC(CH_2PPh_2)_3$].[10h] The C−S insertion product is actually the 2-vinylthiophenolate complex (triphos)Rh[η^3-S(C_6H_4)CH=CH_2] (**1**) formed by reductive coupling of a terminal hydride ligand with the vinyl moiety of a metallabenzothiabenzene intermediate (Scheme 2).

In this report, we show that **1** is an efficient catalyst precursor, under relatively drastic reaction conditions (30 atm H_2, 160 °C), for the transformation of **BT** into 2-ethylthiophenol (**ETSH**) and to a much lesser extent for the hydrogenation of **BT** to

Scheme 2



DHBT. The catalytic reaction is truly homogeneous and has been studied *in situ* by means of high-pressure NMR spectroscopy.[13] This technique, in combination with the use of isolated complexes in independent reactions, has permitted mechanistic conclusions to be drawn which account for the observed catalytic activity and unambiguously show that, in the transformation of **BT** to **ETSH**, ring-opening of the former substrate occurs prior to hydrogenation.

Experimental Section

General Information. All reactions and manipulatioins were routinely performed under a nitrogen atmosphere by using standard Schlenk techniques. Tetrahydrofuran (THF) was distilled from $LiAlH_4$; acetone was dried over potassium carbonate and then fractionally distilled. The solvents were stored over molecular sieves and purged with nitrogen prior to use. Benzo[*b*]thiophene (**BT**, Aldrich) was sublimed prior to use. 2-Ethylthiophenol (**ETSH**, 90%), styrene (99+%), and $LiHBEt_3$ (1 M solution in THF) were purchased from Aldrich. All other chemicals were commercial products and were used as received without further purification. Literature methods were employed for the synthesis of (triphos)Rh[η^3-S(C_6H_4)CH=CH_2] (**1**),[10h] (triphos)RhH_3 (**5**),[14] [(triphos)Rh{η^4-S(C_6H_4)CH(CH_3)}]BF_4 (**7**),[10h] and [(triphos)Rh(η^2-*C*,*S*-C_8H_6S)]PF_6 (**9**).[15] 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. ^1H NMR spectra were obtained on a Bruker ACP 200 (200.13 MHz) spectrometer. ^1H NMR shifts are recorded relative to the residual ^1H resonance in the deuterated solvent. $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker ACP 200 spectrometer operating at 81.01 MHz. Chemical shifts are relative to external 85% H_3PO_4 with downfield values reported as positive. Broad band and selective $^1H\{^{31}P\}$ NMR experiments were carried out on the Bruker ACP 200 instrument equipped with a 5-mm inverse probe and a BFX-5 amplifier device. The 10-mm sapphire high pressure NMR (HPNMR) tube was designed and constructed at the Anorganisch Chemisch Laboratorium, J. H. van't Hoff Research Institute, Amsterdam; for the design of the titanium pressure head see ref 16. GC analyses were performed on a Shimadzu GC-14 A gas chromatograph equipped with a flame

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(15) The synthesis and characterization of **9** which is structurally analogous to the Ir derivative [(triphos)Ir(η^2-*C*,*S*-C_8H_6S)]BPh_4 authenticated by an X-ray analysis,[10a] will be published elsewhere.

Table 1. Catalytic Hydrogenation Experiments[a]

run no.	solvent	T (°C)	PH_2 (atm)	t (h)	reaction mixture composition (%)[b] ETB	ETSH	BT	DHBT	other	ETSH rate[c]
1	acetone	160	30	2	0.2	25.5	73.2	1.1		12.7
2	acetone	160	30	4	0.2	39.8	57.4	2.6		9.9
3	acetone	160	30	8	0.3	45.1	51.8	2.8		5.6
4	acetone	160	30	12	0.4	51.0	44.6	4.0		4.2
5	acetone	160	30	16	0.4	57.4	37.6	4.6		3.6
6[d]	acetone	160	30	16		57.6	37.9	4.5		3.6
7	THF	160	30	16	0.2	52.8	41.3	5.7		3.3
8	acetone	160	15	16	0.3	55.3	40.2	4.2		3.5
9	acetone	160	60	16	0.4	60.2	34.3	5.1		3.8
10	THF	120	30	4		2.0	97.6	0.4		0.5
11	acetone	100	30	16		1.4	98.1	0.5		<0.1
12	acetone	180	30	16	0.9	64.2	29.0	5.9		4.0
13	THF	220	30	16	3.5	43.3	45.8	6.9	0.5	2.7
14[d]	THF	220	30	16		42.6	51.1	6.0	0.3	2.7
15[e]	acetone	160	30	16	0.4	56.8	38.4	4.4		3.5
16[f]	acetone	160	30	16	0.3	61.2	34.0	4.5		1.9

[a] Reaction conditions: Parr reactor, **1** (0.12 g, 0.139 mmol), BT (1.86 g, 13.9 mmol), solvent (30 mL). [b] Key: ethylbenzene (ETB), 2-ethylthiophenol (ETSH), benzo[*b*]thiophene (BT), dihydrobenzo[*b*]thiophene (DHBT). [c] Rate expressed as mol of ETSH per mol of catalyst per hour. [d] Reaction carried out in the presence of excess elemental Hg. [e] Reaction conditions: Parr reactor, **3** (0.12 g, 0.0695 mmol), BT (1.86 g, 13.9 mmol), solvent (30 mL). [f] Reaction conditions: Parr reactor, **1** (0.12 g, 0.139 mmol), BT (0.93 g, 6.95 mmol), solvent (30 mL).

ionization detector and a 30m (0.25-mm i.d., 0.25-μm 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 hydrogen were performed with a Parr 4565 reactor equipped with a Parr 4842 temperature and pressure controller.

Catalytic Hydrogenation of Benzo[*b*]thiophene. (A) Parr Reactor Experiments. The reaction conditions and the results of these experiments have been collected in Table 1. In a typical experiment, a solution of (triphos)Rh[η^3-S(C_6H_4)CH=CH_2] (**1**) (0.12 g, 0.139 mmol) and a 100-fold excess of **BT** (1.86 g, 13.9 mmol) in acetone (or THF) (30 mL) were placed into the Parr reactor, pressurized with hydrogen to the desired pressure at room temperature, heated to the appropriate temperature, and then immediately stirred. After the desired time, the reactor was cooled to room temperature and slowly depressurized by bubbling the gaseous phase into an aqueous solution of Pb(II) acetate. H_2S eventually released during the reaction led to the formation of the characteristic black precipitate of PbS. The contents of the reactor were transferred into a Schlenk-type flask. A sample of the solution was withdrawn and analyzed by GC and GC/MS. The rest of the solution was concentrated to dryness in vacuo and the residue, dissolved in CD_2Cl_2, was studied by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, which showed the quantitative transformation of **1** into the bis-thiolate complex (triphos)RhH[*o*-S(C_6H_4)C_2H_5]$_2$ (*vide infra*). At temperatures higher than 200 °C only, extensive decomposition of the [(triphos)Rh] moiety occurred to give unknown compounds.

Catalytic reactions were carried out in the presence of excess elemental Hg (1000:1) to test the homogeneous character of the reactions. (Note: The reliability of the Hg test to demonstrate the homogeneity of a reaction is not compromised by the presence in the reaction mixture of organic thiols and H_2S).[17]

(B) Sapphire Tube HPNMR Experiments. In a typical experiment, a 10-mm sapphire HPNMR tube was charged with a THF-d_8 (2 mL) solution of **1** (0.05 g, 0.0579 mmol) and **BT** (0.78 g, 5.79 mmol) under nitrogen, pressurized with hydrogen to 30 atm at room temperature, and then placed into a NMR probe preheated at 120 °C. The reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. Spectra (acquisition time 10 min) were recorded every 10 min. A spectrum recorded after ca. 2 h showed two pairs of broad resonances centered at 38 and 2 ppm and at 28 and −25 ppm which were assigned to (triphos)Rh(H)$_2$[*o*-S(C_6H_4)C_2H_5] (**2**) and [(η^2-triphos)Rh{μ-*o*-S(C_6H_4)-C_2H_5}]$_2$ (**3**) (*vide infra*), respectively. After 2 h, the probe was sequentially cooled to 100, 80, 50, and 20 °C, and $^{31}P\{^1H\}$ NMR spectra were recorded at each temperature. A complete sequence of the spectra recorded during this experiment is reported in Figure 1. The NMR signals of **3** gradually decreased in intensity, disappearing completely at 80 °C, while the resonances of **2** increased in intensity and sharpened to give well resolved multiplets [AM_2X spin system, δ 37.8 (P_A, $J(P_AP_M)$ = 25.0 Hz, $J(P_ARh)$ = 114.1 Hz), δ 2.0 (P_M,$J(P_MRh)$ = 80.1 Hz)].

After the spectrum at 20 °C was acquired, the tube was removed from the spectrometer, depressurized to ambient pressure, and replaced in the probe. In the room-temperature $^{31}P\{^1H\}$ NMR spectrum of this sample, the resonances of **2** (30%) were now accompanied by those of a new product of the formula (triphos)RhH[*o*-S(C_6H_4)C_2H_5]$_2$ (**4**) [AM_2X spin system, δ 18.1 (P_M, $J(P_MRh)$ = 102.1 Hz), δ −23.3 (P_A, $J(P_AP_M)$ = 26.5 Hz, $J(P_ARh)$ = 68.0 Hz), 70%, Figure 1e] (*vide infra*). The contents of the tube were then transferred into a Schlenk-type flask. A sample of the solution, withdrawn and analyzed by GC and GC/MS, was found to contain **ETSH** (3.4%), **BT** (96.3%), and dihydrobenzo-[*b*]thiophene (**DHBT**, 0.3%). The remainder of the solution was concentrated to dryness in vacuo, and the residue waws dissolved in CD_2Cl_2. ^1H and $^{31}P\{^1H\}$ NMR spectra of this sample demonstrated the complete conversion of **2** to **4** (Figure 1f). The experiment was repeated twice, giving identical results. Experiments lasting 4 and 6 h gave the same overall ^{31}P NMR picture but increased the conversion of **BT** to both **ETSH** (7.1 and 10.3% respectively) and **DHBT** (0.4 and 0.6% respectively). No traces of ethylbenzene (**EB**) were detected by GC-MS.

The highest temperature investigated (120 °C) represents the technical limit of the HPNMR tube. The use of THF rather than of acetone was due to the much better solubility of **1** in the former solvent.

Attempted Hydrogenation of DHBT. Pure **DHBT** was isolated from a combined mixture of several catalytic hydrogenation reactions of **BT** using the following procedure. The solvent was removed under reduced pressure, and the residue, dissolved in CH_2Cl_2, was chromatographed on a silica column with *n*-pentane as eluant. A solution of **1** (0.12 g, 0.139 mmol) and a 50-fold excess of the resultant **DHBT** (0.94 g, 6.9 mmol) in acetone (30 mL) was placed into a Parr reactor, pressurized with hydrogen to 30 atm at room temperature, heated to 160 °C, and immediately stirred. After 16 h, the reactor was cooled to room temperature and slowly depressurized. The contents of the reactor were transferred into a Schlenk-type flask. A sample of the solution, withdrawn and analyzed by GC and GC/MS, showed no conversion of **DHBT** into **BT** and/or **ETSH**.

Catalytic Hydrogenation of Styrene. A solution of **1** (0.12 g, 0.139 mmol) and a 100-fold excess of styrene (1.59 mL, 13.9 mmol) in THF (30 mL) was placed into a Parr reactor, pressurized with hydrogen to 30 atm at room temperature, heated to 160 °C, and immediately stirred. After 2 h, the reactor was cooled to room temperature and slowly depressurized. The contents of the reactor were transferred into a Schlenk-type flask. A sample of the solution, withdrawn and analyzed by GC and GC/MS, showed the almost complete conversion of styrene into **EB** (99.3%). Traces of **ETSH** were also detected in solution. The remainder of the solution was concentrated to dryness in vacuo, and the residue, dissolved in CD_2Cl_2, was studied by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, which showed the quantitative transformation of **1** into a ca. 1:1 mixture of **4** and (triphos)RhH(CO).[14] When the reaction time was increased to 16 h, (triphos)RhH(CO) (identified by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy), **EB**, and **ETSH** (ca. 100:1, GC) were the final products.

Reactions of 1 with Hydrogen in a HPNMR Tube. A 10-mm sapphire HPNMR tube was charged with a THF-d_8 (2 mL) solution of **1** (0.05 g, 0.058 mmol) under nitrogen and then sequentially pressurized with hydrogen to 1, 5, 15 and 30 atm at room temperature. The reactions were followed by variable-temperature $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. Irrespective of the hydrogen pressure, no reaction occurred at temperatures lower than 60 °C. At 60 °C, a slight conversion (20% in 3 h) to the (*o*-ethylthiophenolate) dihydride complex (triphos)Rh(H)$_2$[*o*-S(C_6H_4)C_2H_5)] (**2**) was observed for a H_2 pressure of 5 atm. Only at pressures of $H_2 \geq 15$ atm, a fast reaction occurred to give quantitative conversion of **1** into **2**. An equilibrium concentration (*ca.* 25%) of the dimer **3** was observed to form at the highest temperature and pressure investigated (120 °C, 30 atm H_2).

Reaction of 1 with H_2 (30 atm) at 160 °C. A solution of **1** (0.12

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g, 0.139 mmol) in acetone (30 mL) was placed into a Parr reactor, pressurized with hydrogen to 30 atm at room temperature, and heated to 160 °C with stirring. After 16 h, the reactor was cooled to room temperature and slowly depressurized. The contents of the bomb were transferred into a Schlenk-type flask. A sample of the solution (10 mL) was filtered through acidic aluminum oxide to remove as much of the metal species present as possible and was then analyzed by GC and GC/MS, which showed the presence of free **ETSH** (*ca.* 15% based on the starting complex, **DHBT** as GC internal reference). The remainder of the solution was concentrated to dryness in vacuo, and the residue, dissolved in CD_2Cl_2, was studied by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, which showed the transformation of **1** into a 1:1.5 mixture of the bis-thiolate **4** and decomposition products of the [(triphos)RhH] fragment (essentially phosphine oxides).

Preparation of [(η^2-triphos)Rh{μ-*o*-S(C_6H_4)C_2H_5}]$_2$ (3). A solution of (triphos)RhH_3 (**5**) (0.22 g, 0.30 mmol) and 2-ethylthiophenol (45 μL, 0.30 mmol) in THF (70 mL) was heated at reflux temperature. After 1 h, the reaction mixture was cooled to room temperature and concentrated to ca. 5 mL under vacuum. The portionwise addition of *n*-heptane (30 mL) led to the precipitation of the μ-thiolate dimer **3** as a brown-yellow solid, which was filtered off, and washed with *n*-pentane. The compound is extremely air-sensitive in both the solid state and solution where slow decomposition occurs even under a nitrogen atmosphere: $^{31}P\{^1H\}$ NMR (THF-d_8) 60 °C, AM_2X spin system, δ 28.0 (d, $J(P_MRh)$ = 169.2 Hz, P_M), −26.6 (s, P_A); 20 °C, two AM_2X spin systems, δ 28.5 (d, $J(P_MRh)$ = 169.6 Hz, P_M), −27.7 (s, P_A), δ 28.1 (d, $J(P_MRh)$ = 169.6 Hz, P_M), −27.8 (s, P_A); −50 °C, AM_2X spin system, δ 28.8 (d, $J(P_MRh)$ = 169.3 Hz, P_M), −29.2 (s, P_A); ^1H NMR (THF-d_8, 20 °C) δ 1.62 (q, J(HH) = 7.3 Hz, CH_2CH_3), 1.60 (q, J(HH) = 7.3 Hz, CH_2CH_3), 0.50 (t, CH_2CH_3), 0.47 (t, CH_2CH_3). Anal. Calcd (found) for $C_{98}H_{96}P_6Rh_2S_2$: C, 68.05 (67.84); H, 5.59 (5.51); Rh, 11.90 (11.79); S, 3.71 (3.59).

A $^{31}P\{^1H\}$ NMR spectrum of **3** in THF-d_8 under nitrogen was acquired in the HPNMR tube at the temperature of the *in situ* catalytic experiment (120 °C). The lineshape and chemical shifts of the NMR signals of **3** were found to be identical with those in the catalytic experiment.

Preparation of (triphos)RhH[*o*-S(C_6H_4)C_2H_5]$_2$ (4). A solution of (triphos)RhH_3 (**5**) (0.22 g, 0.30 mmol) and 20-fold excess of 2-ethylthiophenol (0.90 mL, 6 mmol) in THF (70 mL) was heated at reflux temperature. After 1 h, the reaction mixture was cooled to room temperature and concentrated to dryness under vacuum. The brown yellow residue was washed several times with *n*-pentane and dried in vacuo. ^1H and $^{31}P\{^1H\}$ NMR spectra of this sample showed the clean conversion of **5** to **4**. In spite of the repeated washings, some free 2-ethylthiophenol was found to contaminate the product. Attempts to purify **4** by recrystallization from THF/*n*-pentane led to its conversion to the dimer **3**: $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) AM_2X spin system, δ 17.6 (dd, $J(P_MRh)$ 102.0 Hz, P_M), −23.2 (dt, $J(P_ARh)$ = 67.8 Hz, $J(P_AP_M)$ = 26.1 Hz, P_A). ^1H NMR (CD_2Cl_2, 20 °C): δ −7.63 (dq, $J(HP_A)$ = 193.8 Hz, $J(HP_M)$ = J(HRh) = 8.1 Hz, Rh−*H*), 0.97 (t, J(HH) = 7.3 Hz, CH_2CH_3), 2.4 (partially masked by the methylenic chain protons of triphos, CH_2CH_3); IR ν(Rh-H) 1948 (s) cm^{-1}.

Reaction of 3 with Hydrogen. Hydrogen was slowly bubbled through a CD_2Cl_2 (4 mL) solution of **3** (0.02 g, 0.0116 mmol) at room temperature. After 30 min, a 1-mL sample was transferred to a 5-mm NMR tube under hydrogen. ^1H and $^{31}P\{^1H\}$ NMR spectroscopy showed the complete conversion of **3** to **2**: $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) AM_2X spin system, δ 37.1 (dt, $J(P_AP_M)$ = 25.2 Hz, $J(P_ARh)$ = 114.4 Hz, P_A), 2.0 (dd, $J(P_MRh)$ = 80.1 Hz, P_M); ^1H NMR (CD_2Cl_2, 20 °C) δ −7.61 (AA′XX′YZ spin system, second-order doublet of multiplets, $|J(HP_M) + J(HP_{M'})|$ = 172.5 Hz, $J(HP_A)$ = 13.3 Hz, J(HRh) = 6.5 Hz, Rh-*H*), 1.25 (t, J(HH) = 7.4 Hz, CH_2CH_3), 2.96 (q, CH_2CH_3). After replacing hydrogen in the tube with nitrogen using three freeze−pump−thaw cycles, ^1H and $^{31}P\{^1H\}$ NMR spectroscopy showed the quantitative formation of **3**.

Reaction of 3 with 2-Ethylthiophenol. A solution of **3** (0.02 g, 0.012 mmol) and a 20-fold excess of 2-ethylthiophenol (35 μL, 0.232 mmol) in THF-d_8 (1 mL) at −50 °C was placed into a 5-mm NMR tube under nitrogen and then sealed. The reaction was followed by $^{31}P\{^1H\}$ NMR spectroscopy at 20 °C. Within a few minutes the characteristic resonances of **4** appeared; conversion >90% occurred after ca. 5 h. Afterward, the temperature of the NMR probe was gradually increased to 50, 70, and 90 °C. $^{31}P\{^1H\}$ NMR spectra, recorded at each temperature, showed the gradual reconversion of **4** to **3**. At 90 °C, **4** was detected in a 10% amount.

Reaction of 3 with Carbon Monoxide. Carbon monoxide was bubbled through a CH_2Cl_2 (30 mL) solution of **3** (0.20 g, 0.116 mmol) at room temperature for ca. 30 min. After the solvent was removed under vacuum at room temperature, a yellow solid was obtained, which was characterized by IR and NMR spectroscopy as (triphos)Rh(CO)-[*o*-S(C_6H_4)C_2H_5] (**6**): $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) A_3X spin system, δ 6.9 (d, J(PRh) = 106.7 Hz); ^1H NMR (CD_2Cl_2, 20 °C) δ 1.12 (t, J(HH) = 7.3 Hz, CH_2CH_3), 2.71 (q, CH_2CH_3); IR ν(CO) 1898 (s) cm^{-1}.

Reaction of [(triphos)Rh{η^4-S(C_6H_4)CH(CH_3)}]BF_4 (7) with $LiHBEt_3$. A solution of the known[10h] ethylidenecyclohexadienethione complex **7** (0.03 g, 0.03 mmol) in THF-d_8 (1 mL) was placed into a Teflon-capped resealable NMR tube under nitrogen. The solution was cooled to −70 °C and a 2-fold excess of $LiHBEt_3$ (1 M solution in THF, 60 μL, 0.06 mmol) was added to the tube by syringe. ^1H and $^{31}P\{^1H\}$ NMR spectra, recorded at −70 °C, showed the immediate conversion of **7** to a new product **8** characterized by a ^{31}P NMR AMQX spin system and a broad doublet of triplets at −8.77 ppm in the hydride region of the ^1H NMR spectrum. On standing in solution, even at −70 °C, the product slowly converted to **3**; complete transformation was achieved within ca. 1 h at −50 °C. When $LiHBEt_3$ was added to a THF-d_8 solution of **7** at −70 °C under a hydrogen atmosphere, **2** was the only compound formed in solution. On the basis of its NMR data and chemical behavior, **8** was assigned the formula (triphos)RhH-[η^2-S(C_6H_4)CH(CH_3)]: $^{31}P\{^1H\}$ NMR (THF-d_8, −70 °C) AMQX spin system, δ 36.2 (ddd, $J(P_ARh)$ = 120.2 Hz, $J(P_AP_M)$ = 28.5 Hz, $J(P_AP_Q)$ = 18.2 Hz P_A), 0.1 (dt, $J(P_MRh)$ = 72.5 Hz, $J(P_MP_Q)$ = 26.7 Hz, P_M), −19.2 (ddd, $J(P_QRh)$ = 67.8 Hz, P_Q); ^1H NMR (THF-d_8, −70 °C) δ −8.77 (br dt, $J(HP_{trans})$ = 201.5 Hz, $J(HP_{cis})$ = 12.7 Hz, J(HRh) < 5 Hz, Rh-H).

Reaction of [(triphos)Rh(η^2-*C*,*S*-C_8H_6S)]PF_6 (9) with $LiHBEt_3$. A solution of the rhodabenzothiabenzene complex **9**[15] (0.03 g, 0.03 mmol) in THF-d_8 (1 mL) was placed into a Teflon capped resealable NMR tube under nitrogen. The solution was cooled to −70 °C and a 2-fold excess of $LiHBEt_3$ (1 M solution in THF, 60 μL, 0.06 mmol) was syringed into the tube. The ^1H and $^{31}P\{^1H\}$ NMR spectra, recorded at −70 °C, showed the immediate conversion of **9** to **1** with no detection of intermediate species.

Results and Discussion

Catalytic Conversion of BT to ETSH. HPNMR and Autoclave Experiments. When a THF solution of **1** is pressurized with 30 atm of H_2 in a high-pressure NMR (HPNMR) tube in the presence of a 100-fold excess of **BT**, no transformation of the latter substrate is observed before a reaction temperature of 100 °C is reached. Significant conversion (*ca.* 3%) of the added **BT** to **ETSH** occurs at 120 °C after 2 h (GC-MS). Under these conditions, the amount of **ETSH** produced increases with time at an almost constant rate at *ca.* 3% every 2 h. (The longest NMR experiment was performed for an overall experimental time of 6 h, after which time the reaction was quenched by cooling to room temperature and depressuring.)

$^{31}P\{^1H\}$ HPNMR spectra in THF-d_8 were acquired every 10 min and showed already with the first spectrum, the complete transformation of **1** into two species characterized by broad signals at 38 and 2 and 28 and −25 ppm, respectively (trace a in Figure 1). By comparison with the ^{31}P NMR spectra of authentic specimens (*vide infra*) acquired at the same temperature and the same NMR tube, these two species have unambiguously been identified as the (*o*-ethylthiophenolate) dihydride complex (triphos)$Rh(H)_2$[*o*-S(C_6H_4)C_2H_5)] (**2**) and the dimer [(η^2-triphos)Rh{μ-*o*-S(C_6H_4)C_2H_5}]$_2$ (**3**), respectively. The broadness of these NMR signals is due simply to the experimental temperature which, being much higher than the

boiling point of the solvent, causes extensive turbulence in the NMR tube as shown by variable-temperature spectra (*vide infra*).

After 2 h at a constant temperature of 120 °C, the internal temperature of the spectrometer was decreased stepwise to 100, 80, 50, and 20 °C. At each temperature a $^{31}P\{^1H\}$ NMR spectrum was acquired (traces b−d of Figure 1). A decrease of the temperature to 100 °C results in an increase of the concentration of **2** at the expense of **3**. The latter compound disappears completely in the reaction mixture by the time 80 °C is reached (trace c of Figure 1), while the NMR signals of **2** resolve perfectly into a canonical AM_2X spin system with δP_A 37.8, δP_M 2.0, $J(P_AP_M) = 25.0$ Hz, $J(P_ARh) = 114.1$ Hz, $J(P_MRh) = 80.1$ Hz.

After the probe was cooled to 20 °C, the HPNMR tube was depressurized to 1 atm of H_2. A $^{31}P\{^1H\}$ NMR spectrum shows the partial conversion (70%) of **2** to the new (bis-thiolate) hydride complex (triphos)RhH[*o*-S(C_6H_4)C_2H_5]$_2$ (**4**) (*vide infra*). The latter compound is the only species present in solution after all the hydrogen in the HPNMR tube has been replaced with nitrogen. The contents of the HPNMR tube were analyzed by GC-MS, which showed the conversion of *ca.* 3% of **BT** to **ETSH**, plus traces of **DHBT** (*ca.* 0.3%).

An identical ^{31}P NMR picture, but with increased conversion of **BT** to **ETSH** (*ca.* 10%), was observed for an experiment lasting 6 h.

In light of the HPNMR experiments, which are clearly consistent with a catalytic transformation of **BT**, a Parr reactor was charged with a mixture of **1** and **BT** (1:100 ratio) dissolved in acetone (or THF) and pressurized with 30 atm of H_2. The mixture was stirred for a desired time at a constant temperature of 160 °C and then quenched as described in the Experimental Section. After each run, the resulting limpid, yellow orange solution was analyzed by GC-MS. After all of the solvent was removed under reduced pressure, a solid residue was obtained which was characterized by NMR spectroscopy.

The results obtained for different reaction times and in acetone solution are reported in Table 1 (runs 1−5) and show that **1** behaves as a catalyst precursor for the opening and hydrogenation of **BT** to **ETSH**. The observed trend of conversion shows that the rate of **BT** opening and hydrogenation to **ETSH** is initially quite fast and then slows down as the concentration of **BT** decreases, as confirmed by a reaction carried out with half the initial concentration of **BT** (run 16).

The reaction is not fully selective as some **DHBT** and traces of **EB** are also formed (4.6 and 0.4% respectively for a reaction time of 16 h). The occurrence of HDS of **BT**, indicated by the formation of **EB**, is confirmed by the detection of H_2S. Unlike the hydrogenation of **BT** to **DHBT** which, although slowly, increases with time (from 2.6% in 4 h to 4.6% in 16 h), the concentration of the HDS product remains practically constant over 16 h.

Substitution of THF for acetone affected neither the reaction rate nor the product distribution. The terminal metal product of all reactions was unambiguously identified as the bis-thiolate complex **4**. Indeed, no trace of either other phosphorus-containing complexes or free triphos was detected by NMR spectroscopy.

Two reactions lasting 16 h were carried out in the presence of a large excess (1000:1) of elemental Hg.[17] Consistent with a truly homogeneous process, both reactions gave the same results as the analogous reactions performed in the absence of Hg (as far as the conversion of **BT** to **ETSH** and **DHBT** is concerned). In contrast, the formation of **EB** and H_2S was totally depressed by the presence of Hg, which indicates that the desulfurization reaction is heterogeneous in character.

In accord with the HPNMR evidence, reactions carried out at 120 and 100 °C (runs 10−11) gave much lower conversions of **BT** than analogous runs at 160 °C . Increasing the temperature to 180 °C increases the overall transformation of **BT** with no apparent change in the homogeneity of the reaction (run 12). In contrast, at temperatures >200 °C (run 13), the overall conversion of **BT** decreases, while the production of **EB** and H_2S increases. Since extensive decomposition of the [(triphos)RhH] moiety occurs above 200 °C to give several unidentifiable products, we believe that under these conditions Rh metal particles may form, and it is these particles which are responsible for the heterogeneous HDS of **BT**. In support to this belief, a reaction at 220 °C carried out in the presence of elemental Hg produced neither **EB** nor H_2S (run 14).

The influence of the H_2 pressure on the rate of transformation of **BT** was tested with reactions performed at 15 and 60 atm of H_2 (runs 8−9). A comparison with analogous reactions at 30 atm shows that the product composition is practically unaffected by the H_2 pressure in the range investigated, but there is a slight increase in the overall conversion of **BT** to both **ETSH** and **DHBT** as the H_2 pressure is increased.

Finally, a 16-h reaction was carried out using the dimer **3** as the catalyst precursor (run 15), and this reaction gave a similar conversion and product composition as that of an analogous reaction catalyzed by **1**.

Catalytic Hydrogenation of Styrene to Ethylbenzene. A low but significant production of **DHBT** is observed in the course of the hydrotreating of **BT** catalyzed by **1**. Since the formation of **DHBT** increases with time, one can conclude that two independent catalysis cycles are operative, and this was confirmed by an independent reaction in which DHBT was substituted for **BT**. In conclusion, although the predominant reaction is the opening and hydrogenation of **BT** to **ETSH**, hydrogenation of the C_2-C_3 double bond of **BT** also occurs.

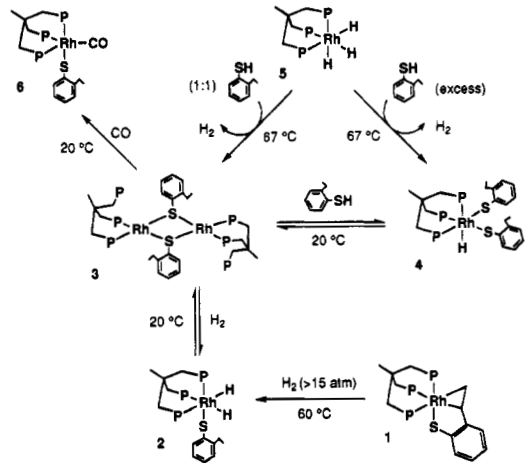
In order to verify the ability of the present rhodium system to catalyze the hydrogenation of double bonds, a reaction was carried out using styrene as substrate under comparable conditions (THF, 30 atm H_2, 160 °C, 100:1 substrate to catalyst ratio). All of the styrene was completely consumed after only 2 h to give **EB**. The terminal metal product of the reaction is an ca. 1:1 mixture of **4** and the hydride carbonyl (triphos)RhH(CO).[14]

When the hydrogenation reaction was carried out under identical conditions for 16 h, the only terminal rhodium product was the hydride carbonyl (triphos)RhH(CO), while a GC-MS analysis of the solution showed the presence of an equivalent amount of free **ETSH** (based on **1**). The formation of the hydride carbonyl complex is not surprising as this compound is invariably obtained by thermolysis of the trihydride (triphos)-RhH_3 in THF at temperatures >120 °C.[18] Thus, the formation of the hydride carbonyl is consistent with the thermal elimination of **ETSH** from **2** at 160 °C to generate the unsaturated [(triphos)-RhH] fragment, which then cleaves THF. The capability of **2** to lose **ETSH** as a thermal step in solution has been confirmed by the hydrogenation of **1** in acetone at 160 °C and 30 atm of H_2 (*vide infra*).

Independent Syntheses and Characterization of the Rhodium Complexes Detected by NMR Spectroscopy during the Course and at the End of the Catalytic Reactions. The only metal species which have been detected by $^{31}P\{^1H\}$ NMR

(18) Bianchini, C.; Meli, A.; unpublished results. It may be anticipated here that the formation of the hydride carbonyl complex proceeds *via* a double hydrogen abstraction from THF to give a carbene intermediate which undergoes thermal decomposition (see: Gutiérrez, E.; Monge, A.; Nicasio, M. C.; Poveda, M. L.; Carmona, E. *J. Am. Chem. Soc.* **1994**, *116*, 791 and Boutry, O.; Gutiérrez, E.; Monge, A.; Nicasio, M. C.; Pérez, P. J.; Carmona, E. *J. Am. Chem. Soc.* **1992**, *114*, 7288).

Scheme 3



spectroscopy during the course of the catalytic transformation of **BT** are the dihydride **2** and the dimer **3**, while the terminal product, upon cooling and depressurizing, is the bis-thiolate complex **4**. All these species have been prepared by independent procedures, as summarized in Scheme 3.

The dimer **3** can be isolated as an analytically pure, brown-yellow solid by treatment of the trihydride (triphos)RhH_3 (**5**)[14] with 1 equiv of **ETSH** in refluxing THF in an open reactor under nitrogen so as to eliminate the evolved H_2. Compound **3** is air-sensitive and thus needs to be handled with extreme care to avoid decomposition. Compound **3** has been assigned a dimeric structure in which two equivalent Rh(I) centers, each of which is in a square-planar environment, are held together by the sulfur atoms of two *o*-ethylthiophenolate bridges. The coordination around each rhodium is completed by a bidentate triphos ligand. This dimeric structure has been unequivocally demonstrated by ^{31}P NMR spectroscopy, and which also shows that this complex exists as two geometric isomers in solution. A sequence of $^{31}P\{^1H\}$ NMR spectra in the temperature range from 20 to 120 °C is shown in Figure 2 (traces a–e); also included is trace a of Figure 1, labeled here as trace f.

At room temperature, two species are clearly present in the spectrum, each of which characterized by a high-field singlet (1P) (δP_A −27.7, −27.8) and by a low-field doublet (2P) (δP_M 28.5, 28.1). The doublet multiplicity is due to coupling of the P_M phosphorus nuclei of each complex to ^{103}Rh with an identical *J* value of 169.9 Hz. The position of P_A as well as the absence of coupling to both P_M and Rh are clearly consistent with the presence of a free phosphine arm of the triphos ligand in **3**, as has been previously observed for other metal complexes in which triphos behaves as a bidentate ligand.[19] On increasing the temperature, all signals extensively broaden so that by 60 °C, the spectrum consists of a doublet and a singlet. At 120 °C, further broadening is observed which makes the $^{31}P\{^1H\}$ NMR spectrum of isolated **3** identical with the spectrum observed under catalytic conditions by HPNMR.

Two hypotheses can be put forward to explain the existence of two isomeric forms of **3**. The most straightforward interpretation is to envision the inversion at the sulfur atom of the bridging thiolate ligands being enough slow on the NMR time scale so as to allow the detection of two isomers at room temperature.[20] A mechanism of this type has previously been reported for various μ-thiolate binuclear metal complexes.[21] Alternatively, different orientations of the free phosphine arm (mutually *cis* or *trans*) may account for the existence of two geometric isomers of **3**.[22]

Whatever the reason for this isomeric phenomenon, that **3** exists in two *geometric* isomers is unequivocally demonstrated by the reactions of **3** with H_2, **ETSH**, or CO (Scheme 3). In fact, these reactions give a unique mononuclear Rh adduct in quantitative yield. The reactions of **3** with H_2 or **ETSH** represent alternative procedures to prepare **2** and **4**, respectively. However, while **4** can be isolated as a brown solid, **2** is stable only in solution under a positive H_2 pressure. Substitution of N_2 for H_2 rapidly regenerates **3**.

Compounds **2** and **4** belong to a family of numerous octahedral Rh(III) and Ir(III) complexes with the general formula (triphos)$M(H)_2L$[23] and (triphos)$MH(L)_2$,[23a-c] respectively (L = unidentate ligand). Thus a detailed description of the chemical-physical properties of **2** and **4** is not warranted here. For the same reason, the spectroscopic characterization of the Rh(I) carbonyl (triphos)Rh(CO)[*o*-$S(C_6H_4)C_2H_5$] (**6**), obtained by reaction of **3** with CO, does not require a detailed discussion.[23a,24]

In addition to various synthetic procedures to **2**, **3**, and **4**,

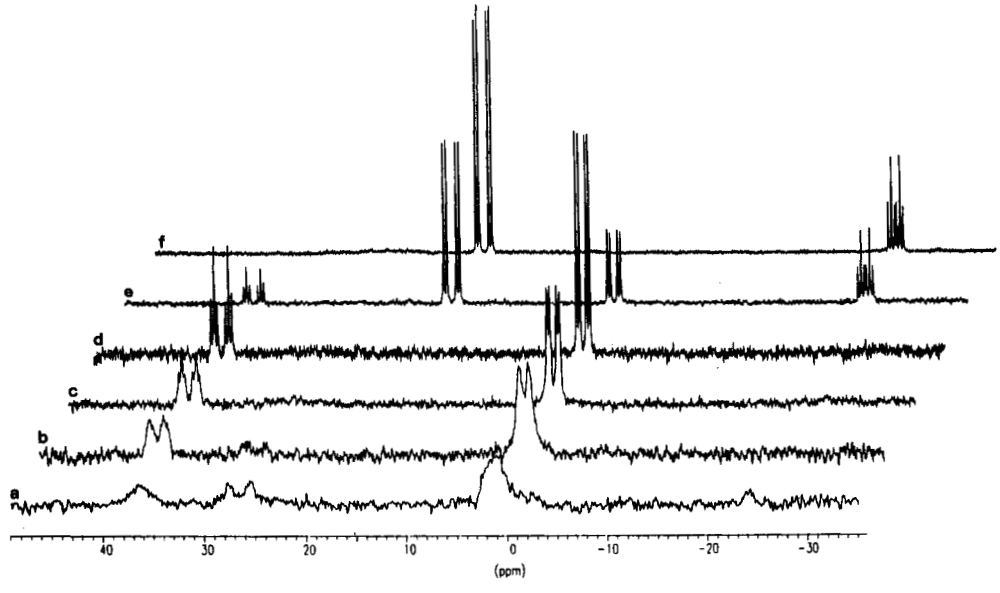


Figure 1. $^{31}P\{^1H\}$ HPNMR study (sapphire tube, THF-d_8, 81.01 MHz) of the catalytic hydrogenation of **BT** in the presence of **1** (30 atm H_2, substrate/catalyst ratio 100): after 4 h at 120 °C (a); (b–d) after the NMR probe was sequentially cooled to 100 (b), 80 (c), 20 °C (d); after the tube was depressurized to 1 atm of H_2 (20 °C, e); after all hydrogen was replaced by nitrogen (20 °C, f).

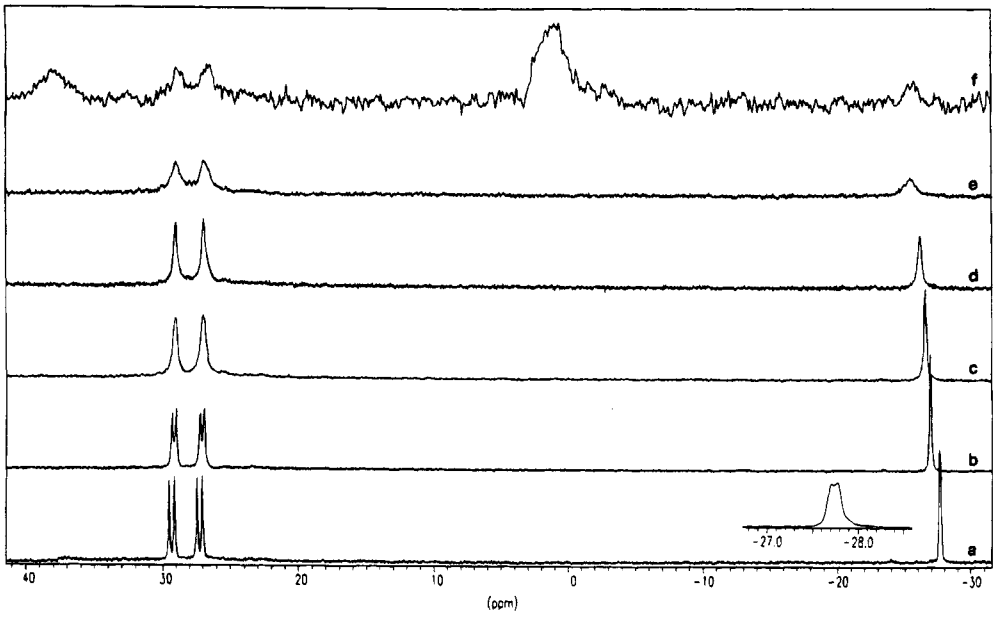


Figure 2. $^{31}P\{^1H\}$ NMR spectra (THF-d_8, 81.01 MHz) of **3** recorded in the temperature range from 20 to 120 °C (traces a−e); for comparative purposes, trace a of Figure 1 is reproduced here as trace f.

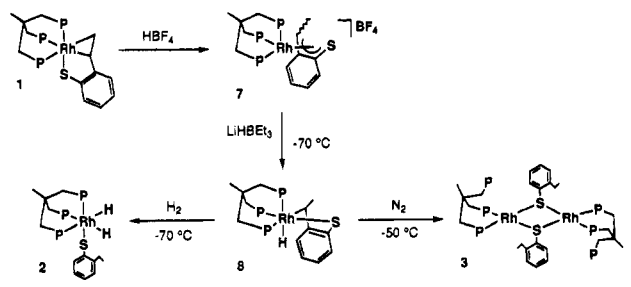
Scheme 3 shows the reactivity pattern which correlates the three complexes. In perfect accord with the results of the catalytic reactions, the bis-thiolate complex **4** is stable only in the presence of an excess of **ETSH**, while the dihydride **2** is stable only under a positive dihydrogen atmosphere. The dimer **3**, and consequently the unsaturated monomeric unit [(triphos)-Rh{*o*-S(C_6H_4)C_2H_5}], can form thermally from either **4** or **2** by reductive elimination of **ETSH** and H_2, respectively. Interestingly, a spectroscopically pure sample of **2** was found to convert partially into **3** *via* H_2 elimination, even under 30 atm of hydrogen, at temperatures >100 °C.

Reaction of the 2-Vinylthiophenolate Complex 1 with H_2. The 2-vinylthiophenolate complex **1** is stable in THF or acetone solution at 60 °C under 1 atm of H_2. A slight conversion (20% in 3 h) to the (*o*-ethylthiophenolate) dihydride complex **2** is observed as the H_2 pressure is increased to 5 atm. Only at pressures >15 atm does the transformation of **1** into **2** occur quantitatively within a few minutes, as shown by HPNMR experiments (Scheme 3). From a stoichiometric point of view, the transformation of **1** into **2** requires the use of 2 equiv of H_2 and thus comprises at least two distinct reaction steps.

In an attempt to gain insight into the mechanism of hydrogenation of **1** to **2**, the former complex has sequentially been reacted with H^+ and H^- to mimic the addition of 1 equiv of H_2.

Treatment of **1** in THF with 1 equiv of HBF_4·OEt_2 yields the known ethylidenecyclohexadienethione complex [(triphos)Rh-{η^4-S(C_6H_4)CH(CH_3)}]BF_4 (**7**) with unknown stereochemistry at the ethylidene substituent (Scheme 4).[10h] Reaction of the latter complex with H^- from $LiHBEt_3$ was carried out in THF-d_8 at low-temperature (−70 °C) and followed by NMR spectroscopy. After adding *super hydride* by syringe, **7** is immediately converted into a new complex bearing a terminal hydride ligand *trans* to a P atom of triphos (doublet of broad triplets at −8.77 ppm with $J(HP_{trans})$ = 201.5 Hz, $J(HP_{cis})$ = 12.7 Hz, J(HRh) = <5 Hz). Although difficult to characterize due to its instability in solution even at −70 °C (see below), the new hydride complex can confidently be assigned to formula (triphos)RhH[η^2-S(C_6H_4)CH(CH_3)] (**8**) by analogy with the isolated iridium derivative (triphos)IrH[η^2-S(C_6H_4)CH(CH_3)] similarly obtained by hydride addition to the ethylidenecyclohexadienethione complex [(triphos)Ir{η^4-S(C_6H_4)CH(CH_3)}]-BF_4.[10a]

Scheme 4



Complex **8** in THF-d_8 slowly converts to the dimer **3** even at −70 °C, while complete conversion takes place at −50 °C in 1 h. This isomerization can conceivably proceed by reductive coupling of the terminal hydride ligand with the metalated alkyl substituent in the thio-ligand. As a result, the unsaturated fragment [(triphos)Rh{*o*-S(C_6H_4)C_2H_5}] forms and then rapidly dimerizes to **3**. The dimerization to **3** is prevented when the reaction between **7** and $LiHBEt_3$ is carried out in the presence of 1 atm of H_2, which results in the selective formation of the dihydride **2**.

In view of the results presented in Scheme 4, it is reasonable to conclude that (i) the conversion of **8** to **2** proceeds through the intermediacy of the Rh(I) fragment [(triphos)Rh{*o*-S(C_6H_4)-

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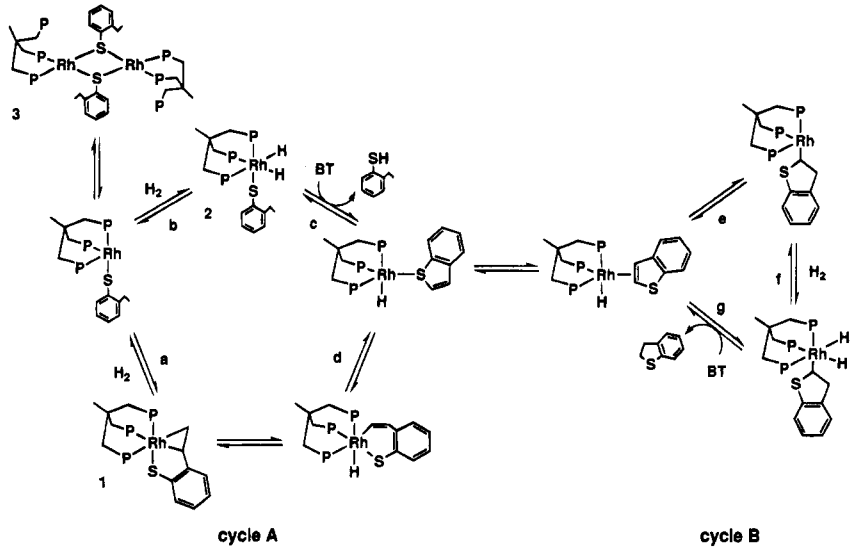
Scheme 5



C_2H_5}], which oxidatively adds H_2; (ii) in the stepwise hydrogenation of **1** to **2**, the higher activation energy process is the first H_2 uptake by **1** to give **8**; and (iii) the hydrogenation of **8** to **2** may proceed *via* heterolytic splitting of H_2 as already suggested for the analogous Ir system.[10a]

Compound **2** is fully stable in acetone solution under 30 atm of H_2 at temperatures as high as 100 °C. Above 100 °C, **2** partially transforms into the dimer **3** (an equilibrium concentration of *ca.* 25% of **3** can be calculated by ^{31}P NMR integration in the HPNMR tube). At the temperature and pressure of the catalytic experiments (160 °C, 30 atm H_2), **2** can also lose **ETSH**. This latter reaction has been shown by GC analysis as well as by the composition of the solid residue of a 16-h reaction (which consisted of a 1:1.5 mixture of the bis-thiolate **4** and decomposition products of [(triphos)RhH]). Unlike THF, acetone, is not capable of trapping the unsaturated [(triphos)-RhH] fragment, which thus can oxidatively add 2 equiv of **ETSH** to give **4**.

Conclusions

Incorporation of all of the above experimental evidence leads to the mechanism shown in Scheme 5 for the reaction between **BT** and H_2 (15−60 atm) catalyzed by **1** in the temperature range from 120 to 180 °C where the system is homogeneous.

Initially, the 2-vinylthiophenolate ligand in **1** is hydrogenated to 2-ethylthiophenolate (step a). As shown in Scheme 4, this process most likely involves the intermediacy of the hydride **8**, which rapidly converts to the fragment [(triphos)Rh{*o*-S(C_6H_4)-C_2H_5}] *via* reductive coupling of the hydride with the metalated alkyl substituent in the thioligand. Reaction of this unsaturated Rh(I) fragment with H_2 then gives the dihydride **2**. At the working temperature of 160 °C, **2** can reductively eliminate either H_2 or **ETSH**. The reductive elimination of H_2 results in the formation of an equilibrium concentration of the dimer **3**, which is inactive toward **BT** (HPNMR evidence). The slight increase in the overall conversion of **BT** observed on going from 15 (60%) to 60 atm of H_2 (66%) may thus simply be due to a larger concentration of the dihydride **2** and the highest pressure. The dihydride **2**, in fact, is the species which, upon reductive elimination of **ETSH**, may interact with **BT** (step c). As independently shown, **2** can lose **ETSH** in THF or acetone solution at temperatures higher than 100 °C to generate the unsaturated fragment [(triphos)RhH]. The elimination of **ETSH** from **2** is greatly accelerated by increasing the temperature and also by interaction with **BT** which stabilizes the unsaturated Rh(I) fragment through the formation of an η^1-*S* adduct (step c). It is generally agreed that adducts of this type play a crucial role in the C−S bond cleavage of thiophenic molecules by metal species.[10b,25] In fact, η^1-*S*-thiophenes are activated in such a way that C−S insertion may follow by attack by the metal (generally electron-rich as in the present case) on the adjacent carbon atom (*via* electron-donation into the C−S antibonding orbital).[10b,25] Step d illustrates this process, which leads to the formation of a rhodabenzothiabenzene hydride intermediate (Scheme 2). This intermediate is unstable[26] and rapidly converts to **1** *via* a simple reductive coupling reaction so that a new catalysis cycle for the opening and hydrogenation of **BT** can begin (cycle **A**).

In addition to **ETSH**, which is the predominant product, all reactions give a small but greater than stoichiometric amount of **DHBT**. The latter substrate is stable under the reaction conditions, and thus its formation can be attributed to a parallel catalysis cycle. A mechanism accounting for the production of **DHBT** is proposed in Scheme 5 (cycle **B**). Cycle **B** requires that the η^1-*S*-**BT** intermediate is in equilibrium with an η^2-2,3-**BT** isomer. Actually, the capability of **BT** to coordinate unsaturated metal systems as equilibrium mixtures of η^1-*S*- and η^2-2,3-isomers has already been demonstrated by Angelici for $Cp(CO)_2Re(BT)$.[9g−i] As reported by Sánchez-Delgado,[11] Fish,[12] and Angelici,[9h] the double bond of **BT** in the η^2-2,3 coordination mode is activated for accepting a migrating hydrogen to give an alkyl intermediate (step e). Reductive elimination with another hydrogen coming from an H_2 oxidative addition step ultimately gives the DHBT product (step g). This metal-catalyzed olefin hydrogenation mechanism is quite familiar in the [(triphos)RhH] system, which, in fact, is an excellent catalyst for the hydrogenation of styrene (herein described) as well as for a variety of other alkenes.[23a]

Angelici has recently shown that the equilibrium η^1-*S*- and η^2-2,3-**BT** isomeric complexes may be affected by both electronic (the η^2-2,3 bonding mode being favored by electron-

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(26) In order to verify that the rhodabenzothiabenzene hydride complex is a precursor to **1** as shown in Scheme 2, the cationic rhodabenzothiabenzene complex [(triphos)Rh(η^2-*C*,*S*-C_8H_6S)]PF_6[15] (**9**) in THF was reacted with $LiHBEt_3$ at −70 °C (see Experimental Section). Even at this low temperature, the formation of **1** was immediate, and no intermediate was seen by ^{31}P NMR spectroscopy.

rich metal centers) and steric (the η^1-*S* bonding mode being favored by substituents on the **BT**) effects.[9g-i] In the case at hand, the rhodium center is sufficiently electron-rich to bind **BT** *via* its olefinic bond, but the large steric crowding provided by the six phenyl groups of triphos probably tips the balance in favor of the η^1-*S* coordination and ultimately makes the opening of **BT** (cycle **A**) largely predominant over the hydrogenation to **DHBT** (cycle **B**).

In the mechanistic picture proposed above, the *real* catalyst for both reactions is the 16-electron fragment [(triphos)RhH] generated from the dihydride **2** by reductive elimination of **ETSH**. This process is apparently the rate determining step in light of the HPNMR evidence as well as the observed dependence on both hydrogen pressure and substrate concentration.

The overall results presented here clearly define homogeneous metal catalysts as viable models for the first steps in the heterogeneously catalyzed HDS reactions. It has unambiguously been shown that the hydrogenation of **BT** to **ETSH** at the [(triphos)RhH] fragment occurs only after the substrate has been C−S inserted, although the straightforward hydrogenation to **DHBT** is also possible as a minor, parallel path. This insertion occurs because the initial stage of the transformation of **BT** is the coordination to the rhodium center *via* either the sulfur or the C_2-C_3 olefinic bond. We suggest that the η^1-*S* and η^2-2,3-**BT** isomers are in equilibrium with each other, but the η^1-*S* intermediate prevails over the η^2-2,3 isomer for steric reasons, thus determining the chemoselectivity of the reaction.

In the future, we shall focus on the last step of the HDS process, namely the catalytic C−S bond cleavage by H_2 to give H_2S and hydrocarbon. Actually, although **EB** and H_2S are produced in some of the catalytic reactions reported in this work, unequivocal evidence has been provided for their heterogeneous origin due to decomposition of the rhodium complex at temperatures >200 °C. Since homogeneous HDS of dibenzothiophene has recently been achieved using the [(triphos)IrH] system as catalyst,[23e] it is expected that kinetically inert transition metals such as those of the third row may provide better model compounds for the HDS of thiophenic molecules.

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