Liquid-Biphase Hydrogenolysis of Benzo[*b*]thiophene by Rhodium Catalysis

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Abstract: The catalytic activity of the zwitterionic complex [(sulphos)Rh(cod)] for the hydrogenation and hydrogenolysis reactions of benzo[*b*]thiophene (BT) has been studied in either methanol or liquid-biphase systems comprising MeOH or MeOH−H_2O as the polar phase and *n*-heptane as the organic phase [sulphos = $^-O_3S(C_6H_4)CH_2C(CH_2PPh_2)_3$]. The catalyst activity is independent of the phase variation. Under neutral conditions, the slow but selective hydrogenation of BT to 2,3-dihydrobenzo[*b*]thiophene is observed. Conversely, in the presence of NaOH or other strong bases, the fast and selective hydrogenolysis of BT to 2-ethylthiophenol sodium salt occurs. In a typical liquid-biphase hydrogenolysis reaction [35 mg (0.035 mmol) of catalyst, 470 mg (3.5 mmol) of BT, 180 mg (4.5 mmol) of NaOH, 5 mL of MeOH, 5 mL of H_2O, 10 mL of *n*-heptane, 30 bar of H_2, 160 °C], all the substrate is practically consumed in ca. 5 h to give the 2-ethylthiophenolate product. The strong base plays a dual role in the hydrogenolysis reaction: it promotes the formation of the Rh−H species (which is necessary for the C−S insertion step) by heterolytic splitting of H_2 and accelerates the conversion of BT by aiding the reductive elimination of the hydrogenolysis product. The effect of the H_2 pressure and of the substrate, catalyst, and base concentrations on the conversion rate of BT has been studied under liquid-biphase conditions. High-pressure NMR experiments in sapphire tubes have provided mechanistic information on the catalysis cycle for the hydrogenolysis of BT in MeOH. Under catalytic conditions, the phosphorus-containing rhodium compounds (visible on the NMR time scale) are the trihydride [(sulphos)RhH₃]⁻ and the dihydride 2-ethylthiophenolate complex [(sulphos)Rh(H)₂(*o*-S(C_6H_4)C_2H_5)]⁻. Consistent with previous studies, the reductive elimination of the thiol from the metal center is suggested to be the rate-determining step of the hydrogenolysis reaction of BT catalyzed by the 16e⁻ fragment [(sulphos)RhH]⁻.

Introduction

Considering the current world production of petroleum, its hydroprocessing is probably the largest volume industrial application of transition-metal catalysis. In this procedure, fossil fuel feedstocks are treated with a high pressure of hydrogen (35−170 bar) over hot heterogeneous catalysts (300−425 °C) to remove sulfur, nitrogen, and residual metals prior to further processing.[1]

Sulfur in fossil materials is contained in various organic compounds, which include thiols, sulfides, disulfides, and the more refractory thiophenes, benzothiophenes, and dibenzothiophenes. The removal of sulfur from fossil materials is commonly referred to as hydrodesulfurization (HDS). There are two major reasons for reducing sulfur levels in petroleum feedstocks: (i) to minimize the amounts of sulfur introduced into the atmosphere by combustion of petroleum-based fuels (contribution to acid rain) and (ii) to prevent the poisoning of reforming and cracking catalysts that are used to upgrade feedstocks to product fuels.[2]

Although HDS is routinely carried out in oil refineries worlwide, a clear need exists for more active catalysts capable of removing a greater proportion of sulfur. Also, different refined fuels contain different types of organosulfur compounds, and thus more specific catalysts for each type of feedstocks need to be developed.

The commercial HDS catalysts are generally prepared by coimpregnation of Mo or W salts on a *γ*-alumina support, followed by sulfidation with H_2S/H_2. Increased efficiency is achieved by introduction of late transition metals like Co, Ni, Ru, Rh, and Ir as promoters.[3] According to a recent mechanistic interpretation,[4] the active centers for the activation of the thiophenic molecules are just the promoter atoms located at the edge plane of a MoS_2 (or WS_2) single slab, whereas H_2 activation occurs on MoS_2 (or WS_2). The key role of the metal promoter in the activation of the thiophenes has also been supported by several homogeneous modeling studies which clearly show that C−S bond scission is almost exclusively brought about by promoter metal complexes.[5] For the following, crucial desulfurization step, however, soluble metal complexes are generally inefficient, unless either W (or Mo) or hydride ligands bound to a second metallic center are comprised in the complex framework.[6−8] In the absence of these two conditions, the ultimate activation of thiophenes by soluble metal complexes seems to be the conversion to thiolate ligands, which may eventually be eliminated as thiols upon treatment with

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H_2.[9-12] Homogeneous catalytic reactions for the hydrogenolysis of thiophene, benzo[b]thiophene, dibenzo[b,d]thiophene, and dinaphtho[2,1-b:1′,2′-d]thiophene have already been reported.[9c,d,13]

The proven capability of promoter metal complexes of catalyzing the hydrogenolysis of thiophenes to thiols under mild reaction conditions suggests an alternative two-step procedure to HDS in which petroleum is firstly treated with H_2 in the presence of a late-transition-metal catalyst and then is hydrogenated over conventional heterogeneous catalysts. These catalysts, in fact, are capable of catalyzing the desulfurization of the thiols under much milder conditions than those currently employed to accomplish the overall HDS of the thiophenic precursors.[2,3]

As reported above, the hydrogenolysis of thiophenes to thiols may not necessarily imply a heterogeneous process, but certainly cannot be performed in the homogeneous phase at the industrial level. The impressive progress recently achieved in the field of water-soluble catalysts, however, paves the way to the application of aqueous biphase catalysis to large volume reactions such as the hydrotreating of distillates.[14] Indeed, a two-step (aqueous biphase/heterogeneous) approach to HDS of thiophenes would have some advantages over conventional heterogeneous processes: (i) Molecular metal catalysts are more amenable to mechanistic studies applying spectroscopy than supported catalysts. Hence, a fine tuning of the liquid-biphase catalyst and of its activity may be anticipated, particularly as regards the design of catalysts specifically tailored for different types of thiophenes. (ii) The application of heterogeneous catalysis to the desulfurization of the thiols allows the use of mild reaction conditions under which the benzene rings of the benzothiophenes and dibenzothiophenes are not affected, and hence a higher octane rating may be obtained. (iii) The direct extraction of the thiol products into the water phase, resulting in the net desulfurization of the fuel, may be a feasible process by addition of bases. On the other hand, disadvantages of the two-step process proposed here may be envisaged in the increased cost as well as its application to very large volume reactions. The economical question may become of secondary importance, particularly for those countries which are rich in very heavy crudes, as one considers that international regulations will soon require reducing the sulfur contents in fuels to less than 100 ppm (60 ppm in some countries).[15] Indeed, this level is not easily attained with the conventional catalysts, even by repeated treatments. The two-step process might thus be convenient for the purification of distillates from residual sulfur up to the limit of commercial fuels.

We have recently reported the synthesis of a zwitterionic rhodium(I) complex, [(sulphos)Rh(cod)] (**1**), that exhibits inherent surface-active attributes [sulphos = $^-O_3S(C_6H_4)CH_2C(CH_2PPh_2)_3$, cod = cycloocta-1,5-diene].[16] This complex is
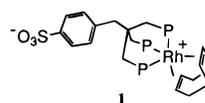
soluble in polar solvents (MeOH or 1:1 (v/v) MeOH−H_2O mixtures) but not in hydrocarbons. However, a 1:1 mixture of MeOH and *n*-heptane containing **1** gives a unique phase already at 60 °C, but at room temperature complete phase separation occurs. In the MeOH−H_2O/*n*-heptane system, **1** behaves as a catalyst precursor for the hydrogenation and hydroformylation of olefins, at the end of which all the rhodium is recovered in the polar phase and the products are found in the hydrocarbon phase.[16]

These properties of **1** prompted us to study its application to the liquid-biphase hydrogenolysis of benzo[b]thiophene, which is one of the most difficult thiophenic substrates to degrade. The results of our study are described here.

Experimental Section

General Information. All reactions and manipulations were routinely performed, unless otherwise stated, under a nitrogen atmosphere by using standard Schlenk techniques. High-pressure, high-temperature reactions under a controlled pressure of hydrogen were performed with a stainless steel Parr 4565 reactor equipped with a Parr 4842 temperature and pressure controller. Tetrahydrofuran (THF) was purified by distillation under nitrogen from LiAlH4. Benzo[b]thiophene (99%, Aldrich) was sublimed prior to use. Potassium *tert*-butoxide (KOBu^t, 95%), methanol, and *n*-heptane were purchased from Aldrich and used without further purification. All the other reagents and chemicals were reagent grade and were used as received by commercial suppliers. The rhodium complex [(sulphos)Rh(cod)] (**1**) was prepared as previously described.[16] Deuterated solvents for NMR measurements (Merck) were dried over molecular sieves. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were obtained on either a Bruker ACP 200 (200.13, 50.32, and 81.01 MHz, respectively) or a Varian VXR 300 (299.94, 75.43, and 121.42 MHz, respectively) spectrometer. All chemical shifts are reported in parts per million (δ) relative to tetramethylsilane, referenced to the chemical shifts of residual solvent resonances (^1H, ^{13}C) or 85% H_3PO_4 (^{31}P). The 10 mm sapphire NMR tube was purchased from Saphikon (Milford, NH), while the titanium high-pressure charging head was constructed at ISSECC-CNR (Firenze, Italy). 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 μm film thickness) SPB-1 Supelco fused silica capillary column. GC/MS analyses were performed on a Shimadzu QP 5000 apparatus equipped

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with a column identical to that used for GC analyses. Elemental analyses (C, H, N) were performed using a Carlo Erba Model 1106 elemental analyzer. Atomic absorption analyses were performed with a Perkin-Elmer 5000 instrument.

Hydrogenation of Benzo[b]thiophene to 2,3-Dihydrobenzo[b]-thiophene. In a typical experiment, the catalyst **1** and benzo[b]-thiophene (BT) were dissolved in the appropriate mixture of deareated organic solvents in a Schlenk flask. The mixture was then transferred under nitrogen into a Parr reactor. In the reactions with water, this was introduced into the reactor in a second step due to the poor solubility of the reaction components in either MeOH–H_2O or MeOH–H_2O/n-heptane at ambient temperature. A total amount of 20 mL of solvents was generally used. After the reactor was pressurized to the desired H_2 pressure at room temperature, the temperature was increased with stirring (650–1800 rpm). After the chosen time, the reactor was gently cooled to room temperature over ca. 1 h (initially by exposure to air, and then, when the internal temperature was lower than 100 °C, by means of an ice–water bath). At this point, the reactor was depressurized (in some experiments the gaseous phase was bubbled into an aqueous solution of $Pb(OAc)_2$ at pH ≅ 4.5 for eventual trapping of H_2S). The reactor was then opened in the air, and its contents were transferred *via* syringe into a flask and analyzed by GC and GC/MS. In the liquid-biphase reactions, each phase was analyzed by GC. Afterward, THF (ca. 30 mL) was added until a unique phase was observed, which was analyzed to obtain the total distribution of products. Selected catalytic reactions were also carried out in the presence of excess elemental Hg (2000:1, 1800 rpm) to test the homogeneous character of the reactions.[17] Upon hydrogenation, the cod ligand in the catalyst precursor was liberated in solution as a mixture of cyclooctene and cyclooctane.

Hydrogenolysis of BT to 2-Ethylthiophenolate. A. Parr Reactor Experiments. The procedure described above for the hydrogenation of BT to 2,3-dihydrobenzo[b]thiophene (DHBT) was followed also for the hydrogenolysis reactions, the only difference being that a basic coreagent (generally NaOH) was used. In a typical experiment, the desired amount of base was introduced into the reactor as a solid prior to the addition of the solvents and reagents. After each catalytic run, the reactor was cooled to room temperature and its contents were collected in a flask containing 1–2 mL of HCl(aq). This acidification step converts the sodium salt of 2-ethylthiophenolate to 2-ethylthio-phenol (ETP). This procedure is necessary to have reliable GC analyses as well as to prevent the base-promoted oxidation of the thiophenolate product to bis(2-ethylphenyl) sulfide. In the case of liquid-biphase reactions, ca. 50 mL of THF was added to obtain a unique phase for GC and GC/MS analyses. Experimental conditions for a typical reaction in the liquid-biphase system MeOH–H_2O/n-heptane are as follows: 35 mg (0.035 mmol) of catalyst, 470 mg (3.5 mmol) of BT, 180 mg (4.5 mmol) of NaOH, 5 mL of MeOH, 5 mL of H_2O, 10 mL of n-heptane, 30 bar of H_2, 160 °C.

In selected experiments carried out in MeOH–H_2O/n-heptane mixtures, the phases were collected without HCl addition. Both phases were analyzed by GC which showed that all the produced thiophenolate accumulates in the polar phase, while the unreacted substrate, eventual byproducts [DHBT, ethylbenzene (EB)], cyclooctane, and cyclooctene remain in the n-heptane phase. The total product distribution was confirmed by analysis of the unique phase obtained by adding HCl and THF. In several biphasic experiments, after the hydrocarbon layer was separated, the solvent was removed in vacuo and the residue was analyzed by ^{31}P NMR spectroscopy and atomic absorption spectrometry. No appreciable amount of either phosphorus compounds or rhodium was detected. Selected catalytic reactions were also carried out in the presence of either an excess of elemental Hg (2000:1, 1800 rpm) or a commercial surfactant of wide use in biphase reactions (Pluronic L101).

S-Methyl-2-ethylthiophenol (METP) is formed as a byproduct already at 160 °C by reaction of sodium ethylthiophenolate with MeOH. The concentration of METP increases with time and temperature. The formation of METP was confirmed by the independent reaction of sodium ethylthiophenolate with MeOH at 200 °C in the absence of Rh catalyst. Data for *S*-Methyl-2-ethylthiophenol: ^1H NMR (CDCl_3, 20 °C) δ 7.2–7.0 (m, 4H, Ph), 2.68 (q, 2H, CH_2CH_3), 2.32 (s, 3H, SCH_3),

1.19 (t, 3H, CH_2CH_3); $^{13}C\{^1H\}$ NMR (CDCl_3, 20 °C) δ 142.5 (C), 137.8 (C), 128.8 (CH), 127.2 (CH), 126.0 (CH), 125.7 (CH), 27.4 (CH_2-CH_3), 16.3 (SCH_3), 15.0 (CH_2CH_3); GC/MS, EIMS, 70 eV, m/e (%) 152 (100) M$^+$, 137 (95) M − Me$^+$, 105 (24) M − SMe$^+$, 91 (22) $C_7H_7^+$, 77 (30) $C_6H_5^+$.

B. Sapphire Tube HPNMR Experiments. A 10 mm sapphire HPNMR (HP = high pressure) tube was charged with a MeOH-d_4 (2 mL) solution of **1** (60 mg, 0.06 mmol) and a 10-fold excess of both BT (80 mg, 0.6 mmol) and KOBu^t (67 mg, 0.6 mmol) under nitrogen, pressurized with hydrogen to 30 bar at room temperature, and then placed into a NMR probe at room temperature. The reaction was followed by variable-temperature $^{31}P\{^1H\}$ NMR spectroscopy. A sequence of selected $^{31}P\{^1H\}$ NMR spectra is reported in Figure 3. The transformation of **1** (trace a, at 20 °C) already occurred at 60 °C, yielding four new sets of resonances (trace b, after 1.5 h), three of which were assigned to [(sulphos)Rh(η^3-S(C_6H_4)CH=CH_2)]$^-$ (**2**), [(sulphos)Rh(H)_2(o-S(C_6H_4)C_2H_5)]$^-$ (**3**), and [(sulphos)Rh(H)_3]$^-$ (**4**). A fourth signal (doublet at 15.0 ppm) is attributed to a rhodium complex of still undefined structure that does not participate in any transformation of BT. Indeed, this species also forms by hydrogenation of **1** in MeOH-d_4 in the presence of KOBu^t (see below) and does not react with either BT or ETP. Compounds **2**−**4** were identified by comparison of their $^{31}P\{^1H\}$ NMR spectra to those of the analogous triphos complexes [(triphos)Rh(η^3-S(C_6H_4)CH=CH_2)] (**2***),[18] [(triphos)Rh(H)_2(o-S(C_6H_4)-C_2H_5)] (**3***),[9c] and [(triphos)Rh(H)_3] (**4***),[19] respectively. Increasing the temperature to 120 °C (a temperature to which the catalysis occurs, see entry 5 in Table 2) led to a considerable increase of the concentration of the thiolate dihydride **3** at the expense of both **2** and **4**. The trihydride did not disappear even for prolonged heating (2 h), which indicated the attainment of a thermostationary state (trace c). After the catalytic reaction was quenched by cooling to room temperature, compounds **2**−**4** were detected in ratios of 33:48:19 (trace d). The tube was then removed from the spectrometer and depressurized to ambient pressure. The contents of the tube were then transferred into a Schlenk-type flask and acidified with HCl(aq). A sample of the solution, withdrawn and analyzed by GC and GC/MS, was found to contain ETP (35%), BT (53%), and DHBT (12%) as mixtures of H/D isotopomers. The following spectroscopic properties are illustrative of compounds **2**−**4**. Data for **2**: $^{31}P\{^1H\}$ NMR AMQX pattern, δ 31.3 (P_A, J(P_AP_M) = 34.0 Hz, J(P_AP_Q) = 32.5 Hz, J(P_ARh) = 108.0 Hz), −0.8 (P_M, J(P_MP_Q) = 48.1 Hz, J(P_MRh) = 116.2 Hz), −9.8 (P_Q, J(P_QRh) = 105.9 Hz). Data for **3**: $^{31}P\{^1H\}$ NMR AM_2X pattern, δ 37.2 (P_A, J(P_AP_M) = 25.2 Hz, J(P_ARh) = 114.6 Hz), 1.8 (P_M, J(P_MRh) = 80.3 Hz); ^1H NMR δ −7.85 (dm, J(HP_trans) = 179 Hz, RhH). Data for **4**: $^{31}P\{^1H\}$ NMR A_3X pattern, δ 22.8 (P_A, J(P_ARh) = 86.1 Hz); ^1H NMR δ −8.68 (dm, J(HP_trans) = 146 Hz, RhH). Due to H/D exchange caused by the MeOH-d_4 solvent, the hydride resonances in the ^1H NMR spectra of **3** and **4** appear as low-intensity, broad signals. The coupling to deuterium similarly affects the $^{31}P\{^1H\}$ NMR resonances of the phosphorus nuclei trans to the hydride ligands.

An analogous variable-temperature HPNMR experiment carried out at higher pressures of H_2 (50−70 bar) showed an identical sequence of products. It was observed, however, that the concentration of the trihydride **4** under catalytic conditions (120 °C) sligtly increases with pressure.

HPNMR Reaction of 1 with H_2, Followed by Sequential Treatment with BT and H_2. A 10 mm sapphire HPNMR tube was charged with a MeOH-d_4 (2 mL) solution of **1** (60 mg, 0.06 mmol) and a 10-fold excess of KOBu^t (67 mg, 0.6 mmol) under nitrogen, pressurized with hydrogen to 30 bar at room temperature, and then placed into a NMR probe at room temperature. The reaction was followed by variable-temperature $^{31}P\{^1H\}$ NMR spectroscopy. A sequence of selected $^{31}P\{^1H\}$ NMR spectra is reported in Figure 4. The reaction of **1** (trace a, at 20 °C) with hydrogen already occurred at 60 °C, yielding almost quantitatively the trihydride **4** (trace b, at 20 °C after 3 h at 60 °C). The tube was depressurized to ambient pressure, and then all the hydrogen was replaced with nitrogen by three freeze/pump/

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Table 1.   Selective Hydrogenation of Benzo[*b*]thiophene Catalyzed by [(sulphos)Rh(cod)][a]

				reaction mixture composition (%)[c]				
entry	solvent	T (°C)[b]	t (h)	BT	DHBT	METP	ETP	EB
1	MeOH	200	17	70	30			
2	MeOH	200	70	50	43	<1		7
3	MeOH−H₂O (1:1, v/v)	200	17	60	38		1	1
4	MeOH−H₂O/*n*-heptane (1:1:2, v/v/v)	175	110	75	24			1

[a] Reaction conditions: catalyst, 35 mg, 0.035 mmol; BT, 470 mg, 3.5 mmol; solvent, 20 mL; H₂ pressure, 30 bar. [b] At 200 °C partial destruction of the catalyst was observed. [c] Key: benzo[*b*]thiophene (BT), 2,3-dihydrobenzo[*b*]thiophene (DHBT), *S*-methyl-2-ethylthiophenol (METP), 2-ethylthiophenol (ETP), ethylbenzene (EB).

thaw cycles. After 10 equiv of solid BT (80 mg, 0.6 mmol) was introduced into the tube, this was placed into the probe and heated to 100 °C for 1 h. After the probe was cooled to room temperature, the quantitative conversion of **4** to **2** was observed (trace c). Finally, the tube was pressurized with hydrogen to 30 bar and then heated to 120 °C. The spectrum, acquired at this temperature after 40 min, showed the conversion of **2** to **3** and **4** (trace d). Trace e shows the spectrum after the probe was slowly cooled to room temperature.

Synthesis of [(sulphos)Rh(η³-S(C₆H₄)CH=CH₂)]⁻ as the Potassium Salt (K2). This synthesis was performed by using a 10 mm sapphire HPNMR tube as a small autoclave. The tube was charged with a MeOH (2 mL) solution of **1** (60 mg, 0.06 mmol) and a 2-fold excess of KOBu^t (13 mg, 0.12 mmol) under nitrogen, pressurized with hydrogen to 30 bar at room temperature, and then placed into a water bath at 60 °C. After 3 h, the tube was cooled to room temperature and depressurized to ambient pressure, and then all the hydrogen was replaced with nitrogen by three freeze/pump/thaw cycles. The tube was then opened under nitrogen, charged with a solution of BT (80 mg, 0.6 mmol) in MeOH, and heated to 100 °C (ethylene glycol/water bath). After 1 h, the tube was allowed to reach room temperature and the contents were transferred *via* syringe into a Schlenk-type flask. After the volatiles were removed under vacuum, the residue was washed with diethyl ether to eliminate the excess BT. A sample of the residue, dissolved in MeOH-d_4 and characterized by ¹H and ³¹P{¹H} NMR spectroscopy, was found to contain **K2** in ca. 90% yield (³¹P{¹H} NMR integration): ³¹P{¹H} NMR (MeOH-d_4, 20 °C), AMQX pattern, δ 31.3 (P$_A$, J(P$_A$P$_M$) = 34.0 Hz, J(P$_A$P$_Q$) = 32.5 Hz, J(P$_A$Rh) = 108.0 Hz), −0.8 (P$_M$, J(P$_M$P$_Q$) = 48.1 Hz, J(P$_M$Rh) = 116.2 Hz), −9.8 (P$_Q$, J(P$_Q$-Rh) = 105.9 Hz); ¹H NMR (MeOH-d_4, 20 °C) δ 3.1 (m, vinyl CH-CHH), 1.61 (m, vinyl CHH); ¹H{³¹P} NMR (MeOH-d_4, 20 °C) δ 3.16 (d, J(H₃H₂′) = 8.6 Hz, J(H₃H₂) = 7.4 Hz, vinyl CH), 3.08 (d, vinyl CHH), 1.61 (d, vinyl CHH).

Catalyst Stability Tests. After a typical hydrogenolysis reaction performed in MeOH−H₂O/*n*-heptane for 5 h under typical conditions (35 mg catalyst, 470 mg of BT, 180 mg of NaOH, 30 bar of H₂, 160 °C), the reactor was depressurized and cooled to room temperature. The reactor was disassembled under a positive pressure of hydrogen for sampling and recharging (NaOH, 180 mg; BT, 470 mg), and then it was repressurized with H₂ to 30 bar and heated to 160 °C. After 5 h, the polar phase was separated and, after acidification, washed twice with 10 mL of *n*-heptane to remove all ETP. The organic phases were collected together and analyzed by GC and GC/MS, showing that 85% of the overall amount of BT (940 mg) had been consumed. The acidic MeOH−H₂O phase, exclusively containing soluble rhodium species and NaCl, was neutralized with NaOH and used for another catalytic run under standard conditions. The analysis of the reaction products showed a decrease of activity of only 30% notwithstanding the treatment of the catalytic phase with excess HCl and its workup in air.

Attempted Hydrogenolysis of DHBT. A solution of 200 mg (1.5 mmol) of DHBT in 10 mL of *n*-heptane was added to a solution of 35 mg (0.035 mmol) of catalyst in 10 mL of MeOH. The mixture was degassed with N₂ and introduced into a degassed Parr reactor containing 60 mg (1.5 mmol) of NaOH. The reactor was pressurized with 30 bar of H₂ and then heated to 200 °C for 19 h. Analysis of the reaction products by GC and GC/MS, after the usual workup, showed no consumption of DHBT.
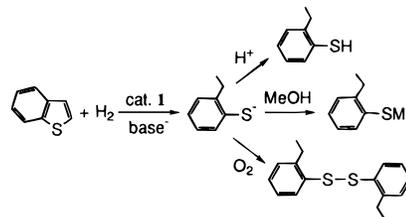
Results

Hydrogenation of Benzo[*b*]thiophene to 2,3-Dihydrobenzo-[*b*]thiophene. All the reactions between benzo[*b*]thiophene

Scheme 1
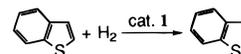
Scheme 2

(BT) and H₂ were carried out in high-pressure reactors in the presence of catalytic amounts of the zwitterionic Rh(I) complex [(sulphos)Rh(cod)] (**1**) (Scheme 1).[16] In a typical homogeneous reaction, the catalyst precursor and the substrate in a 1:100 ratio are dissolved in methanol and the resulting solution is introduced into the reactor under a stream of nitrogen. The reactor is pressurized with hydrogen to 30 bar and then is heated to the desired temperature with stirring.

The results obtained are reported in Table 1. At 200 °C for 17 h, no C−S bond scission of BT occurs, the only reaction product being 2,3-dihydrobenzo[*b*]thiophene (DHBT) in 30% yield (entry 1). Under these conditions, the slow decomposition of the catalyst occurs, however, as shown by the formation of a dark, insoluble material in a reaction lasting 70 h, which converted only 50% of the substrate and also produced an appreciable amount of ethylbenzene (EB) (7%) together with traces of the hydrogenolysis product *S*-methyl-2-ethylthiophenolate (METP) (*vide infra*) (entry 2). The formation of EB is totally suppressed when the reactions are carried out in the presence of a large excess of elemental mercury, consistent with a heterogeneous desulfurization reaction, most likely catalyzed by rhodium particles.[17]

The use of a 1:1 mixture of methanol and water as solvent (entry 3) slightly increases the formation of DHBT (38%) and produces trace amounts of 2-ethylthiophenol (ETP) and EB. The selective formation of DHBT also occurs when the reaction is carried out at 175 °C under biphasic conditions (MeOH−H₂O/ *n*-heptane) (entry 4). At this temperature, no appreciable decomposition of the catalyst is observed, but the rate decreases drastically (25% conversion in 110 h). The DHBT product and the unreacted BT are exclusively found in the *n*-heptane phase, while all the rhodium remains in the polar phase. Irrespective of the phase variation, neither the rate of BT conversion nor the selectivity changes when the stirring rate is increased from 650 to 1800 rpm.

Base-Assisted Hydrogenolysis of Benzo[*b*]thiophene to 2-Ethylthiophenol. The addition of NaOH to the catalytic system dramatically changes the selectivity of the reaction between BT and H₂ and also remarkably accelerates the degradation of the substrate (Scheme 2).

In a first group of experiments, methanol was the solvent of

Table 2. Base-Assisted Hydrogenolysis of Benzo[b]thiophene Catalyzed by [(sulphos)Rh(cod)] at ≤160 °C[a]

entry	solvent	base, mmol	T (°C)	t (h)	reaction mixture composition (%)[b]					cat:base:BT	rate ×10[c]
					BT	DHBT	METP	ETP	EB		
1	MeOH[e]	NaOH, 4.5	160	5	6	1	<1	93	<1	1:130:100	6.5
2	MeOH	KOBu^t, 3.6	160	5	8	1	<1	91	<1	1:100:100	6.4
3[d]	MeOH	NaOH, 4.5	160	16	45	<1	1	53	1	1:540:840	7.4
4[d]	MeOH	NaOH, 9.0	160	16	31	1	1	66	1	1:1100:840	9.2
5	MeOH	NaOH, 4.5	110	288	34	3		63		1:130:100	
6	MeOH−H₂O (1:1, v/v)	NaOH, 4.5	160	5	11	5	<1	84	<1	1:130:100	5.9
7	MeOH/n-heptane (1:1, v/v)[e]	NaOH, 4.5	160	5	4	1	<1	95	<1	1:130:100	6.6
8	MeOH−H₂O/n-heptane (1:1:2, v/v/v)[e]	NaOH, 4.5	160	5	8	2	<1	89	2	1:130:100	6.2
9	MeOH−H₂O/n-heptane (1:1:2, v/v/v)[f]	NaOH, 4.5	160	5	51	2	<1	46	1	1:130:100	3.2

[a] Reaction conditions: catalyst, 35 mg, 0.035 mmol; BT, 470 mg, 3.5 mmol; solvent, 20 mL; H₂ pressure, 30 bar. [b] Key: benzo[b]thiophene (BT), 2,3-dihydrobenzo[b]thiophene (DHBT), S-methyl-2-ethylthiophenol (METP), 2-ethylthiophenol (ETP), ethylbenzene (EB). [c] Average rate expressed as (mmol of ETP) h^{-1}. [d] Reaction conditions: catalyst, 8.2 mg, 0.008 mmol; BT, 940 mg, 7 mmol; solvent, 20 mL; H₂ pressure, 30 bar. [e] This reaction, repeated in the presence of a large excess of elemental mercury (Hg/Rh = 2000), gave identical conversion of BT to ETP and DHBT. [f] Reaction carried out in the presence of the surfactant Pluronic L101.
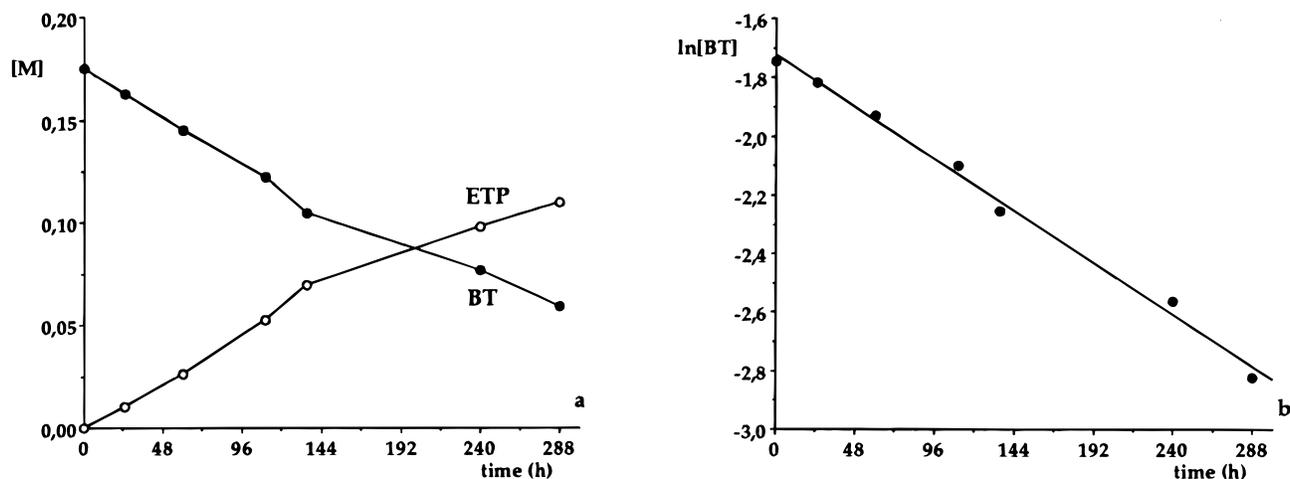

Figure 1. (a) Rate data for the hydrogenolysis of BT catalyzed by **1** in the presence of NaOH at 110 °C (MeOH, 30 bar of H₂, NaOH:BT:**1** = 130:100:1). (b) ln [BT] vs time.

choice (Table 2). Under the conditions employed in the hydrogenation reactions but in the presence of a concentration of NaOH equal to or slightly greater than that of the substrate, almost all BT (94%) is already consumed after 5 h at 160 °C (entry 1). The reaction gives the 2-ethylthiophenolate anion and traces (≤1%) of both DHBT and METP. Almost negligible decomposition of the catalyst occurs as shown by the formation of only trace amounts of EB (*vide infra*). The hydrogenolysis product may be recovered as the sodium salt Na[o-S(C₆H₄)-C₂H₅]; for product identification and quantification, however, it is convenient to transform the thiolate salt into ETP by treatment with aqueous HCl. Accordingly, from now on, the hydrogenolysis product is referred to as ETP. If the final reaction mixture is not acidified, spontaneous oxidation of the thiophenolate product to bis(2-ethylphenyl) sulfide takes place upon exposure to air (Scheme 2).[20] The use of other strong bases such as KOBu^t (entry 2) or KOH affects neither the selectivity nor the activity. Increasing the BT:**1** ratio to 840 does not change the selectivity, but the reaction, although much faster, does not go to completion within 16 h (entry 3) even when a large excess of base is employed (entry 4).

A reaction in methanol was carried out at significantly lower temperature (110 °C, entry 5) at which quite long reaction times are needed to achieve a high conversion (after 288 h, ETP 75%, DHBT 3%). During this experiment, the reaction was periodically sampled (with negligible loss of internal pressure) and the product formation was followed by GC. As is shown in

(20) March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley-Interscience: New York, 1992; pp 1199−1205.

Figure 1, the catalytic activity is maintained over 12 days and a linear plot is obtained by plotting the ln [BT] vs time.

Neither the rate nor the selectivity of the reactions is affected by the use of different solvent mixtures such as MeOH−H₂O (entry 6), MeOH/n-heptane (entry 7), or MeOH−H₂O/n-heptane (entry 8) in the range of stirring rates from 650 to 1800 rpm. Similarly, there is no appreciable change of catalytic activity for reactions carried out in the presence of an excess of elemental mercury, while the addition of an external surfactant decreases the hydrogenolysis rate (entry 9). Reactions in H₂O/n-heptane biphasic systems were unsuccessful, most likely due to the very poor solubility of **1** and BT in water.

Interestingly, in the MeOH/n-heptane or MeOH−H₂O/n-heptane biphase reactions, the hydrogenolysis product is completely found in the polar phase as sodium 2-ethylthiophenolate so as to leave the hydrocarbon phase almost completely desulfurized. No trace of rhodium was found in the hydrocarbon phase by atomic absorption spectrometry.

Increasing the reaction temperature to 200 °C remarkably accelerates the conversion of BT to ETP irrespective of the solvent or mixture of solvents employed (Table 3). Under liquid-biphase conditions (entry 1), all BT is practically consumed in 30 min with formation of ETP and of an appreciable amount of EB (4%). The formation of the latter product is ascribed to increased decomposition of the catalyst at 200 °C. Indeed, when the reaction of entry 1 was carried out in the presence of a large excess of elemental mercury, the production of EB was almost totally suppressed. In the absence of Hg, the concentration of EB increases with time (entry 2),

Table 3. Base-Assisted Hydrogenolysis of Benzo[*b*]thiophene Catalyzed by [(sulphos)Rh(cod)] at 200 °C[a]

				reaction mixture composition (%)[b]				
entry	solvent	base, mmol	*t* (h)	BT	DHBT	MEPT	ETP	EB
1	MeOH−H$_2$O/*n*-heptane (1:1:2, v/v/v)	NaOH, 4.5	0.5	5			91	4
2	MeOH−H$_2$O/*n*-heptane (1:1:2, v/v/v)	NaOH, 3.75	17	1		11	81	7
3	MeOH	NaOH, 3.75	17	3	<1	43	48	6
4	MeOH−H$_2$O (1:1, v/v)	NaOH, 3.75	17	3	<1	13	78	6

a Reaction conditions: catalyst, 35 mg, 0.035 mmol; BT, 470 mg, 3.5 mmol; solvent, 20 mL; H$_2$ pressure, 30 bar. Partial destruction of the catalyst was observed. *b* Key: benzo[*b*]thiophene (BT), 2,3-dihydrobenzo[*b*]thiophene (DHBT), *S*-methyl-2-ethylthiophenol (METP), 2-ethylthiophenol (ETP), ethylbenzene (EB).

Table 4. Base-Assisted Liquid-Biphase Hydrogenolysis of Benzo[*b*]thiophene Catalyzed by [(sulphos)Rh(cod)]: Dependence on Catalyst and Base Concentration[a]

	[cat] (M × 10^3)	[base] (M × 10)	reaction mixture composition (%)[b]					
entry	[mol (L of aq phase)$^{-1}$]	[mol (L of aq phase)$^{-1}$]	BT	DHBT	ETP	EB	cat:base:BT	rate × 10^c
1	3.52	4.50	8	2	89	1	1:130:100	6.2
2	2.76	4.50	29		70	1	0.8:130:100	4.9
3	2.02	4.50	43		56	1	0.6:130:100	3.9
4	1.00	4.50	72		27	1	0.3:130:100	1.9
5	3.52	3.52	18		81	1	1:100:100	5.7
6	3.52	2.24	24		74	2	1:60:100	5.2
7	3.52	1.42	50	1	47	2	1:40:100	3.3
8	3.52	0.72	65	1	33	1	1:20:100	2.3
9	3.52	0.10	84		16	<1	1:3:100	1.1

a Reaction conditions: BT, 470 mg, 3.5 mmol, 3.5 × 10^{-1} mol (L of org phase)$^{-1}$; except entry 9 (KOBu^t) NaOH was employed as base; solvent, 20 mL, MeOH−H$_2$O/*n*-heptane (1:1:2, v/v/v); H$_2$ pressure, 30 bar; temperature, 160 °C; time, 5 h. *b* Key: benzo[*b*]thiophene (BT), 2,3-dihydro[*b*]thiophene (DHBT), 2-ethylthiophenol (ETP), ethylbenzene (EB). *c* Average rate expressed as (mmol of ETP) h^{-1}.

Table 5. Base-Assisted Hydrogenolysis of Benzo[*b*]thiophene Catalyzed by [(sulphos)Rh(cod)]: Dependence on Hydrogen Pressure and Substrate Concentration[a]

	[BT] (M × 10)	PH$_2$ pressure	reaction mixture composition (%)[b]					
entry	[mol (L of org phase)$^{-1}$]	(bar)	BT	DHBT	ETP	EB	cat:base:BT	rate × 10^c
1	3.5	5	61		39	<1	1:130:100	2.7
2	3.5	10	33		66	1	1:130:100	4.6
3	3.5	20	22	1	77	<1	1:130:100	5.4
4	3.5	30	8	2	89	1	1:130:100	6.2
5[d]	3.5	30	4		94	2	1:130:100	6.6
6	3.5	50	13	2	82	3	1:130:100	5.7
7	3.5	70	25	4	68	3	1:130:100	4.8
8	2.1	30	4	1	94	1	1:130:60	3.9
9	4.5	30	14	1	84	1	1:130:130	7.6
10[e]	5.6	30	18	1	80	1	1:160:160	8.9

a Reaction conditions: catalyst, 35 mg, 0.035 mmol, 3.52 × 10^{-3} mol (L of aq phase)$^{-1}$; NaOH, 180 mg, 4.5 mmol, 4.5 × 10^{-1} mol (L of aq phase)$^{-1}$; solvent, 20 mL, MeOH−H$_2$O/*n*-heptane (1:1:2, v/v/v); temperature, 160 °C; time, 5 h. *b* Key: benzo[*b*]thiophene (BT), 2,3-dihydrobenzo[*b*]thiophene (DHBT), 2-ethylthiophenol (ETP), ethylbenzene (EB). *c* Average rate expressed as (mmol of ETP) h^{-1}. *d* Reaction carried out in the presence of excess elemental mercury (Hg/Rh = 2000). *e* NaOH, 220 mg, 5.5 mmol, 5.5 × 10^{-1} mol (L of aq phase)$^{-1}$.

consistent with increased decomposition. At 200 °C, long reaction times result also in the conversion of the 2-ethyl-thiophenolate product to the disulfide METP (11% after 17 h) that accumulates in the hydrocarbon phase. This compound is formed by a noncatalytic reaction between the 2-ethylthio-phenolate anion and MeOH whose rate increases with both the temperature and the MeOH concentration (Scheme 2).[21] Consistently, the analogous reaction in pure methanol (entry 3) gives a greater production of METP as compared to the reactions under biphasic conditions or in a MeOH−H$_2$O mixture (entry 4).

To avoid any decomposition of the catalyst as well as to minimize systematic errors which may be connected with the heating and cooling processes (*ca.* 40 min to reach the working temperature and *ca.* 1 h to cool the reactor), all the subsequent biphasic reactions were carried out under the following conditions: temperature 160 °C, reaction time 5 h, solvent 1:1:2 (v/v/v) MeOH−H$_2$O/*n*-heptane (20 mL). The other reaction parameters (pressure of H$_2$, catalyst concentration, BT concen-

tration, and base concentration) were changed systematically to obtain kinetic information. The results of this investigation are summarized in Tables 4 and 5 and in Figure 2.

As shown in Tables 4 (entries 1−4) and 5 (entries 4 and 8−10), the hydrogenolysis reaction is apparently first-order in both the catalyst and substrate concentration (Figure 2a,b). The average rate (expressed as (mol of ETP) h^{-1}) also increases linearly with the base concentration as long as the base:BT ratio is lower or equal to 0.6 (Table 4, entries 6−9) (Figure 2c). For higher concentrations of base (entries 1 and 5), the rate tends to flatten.

The influence of the H$_2$ pressure on the hydrogenolysis rate is rather complicated (Table 5). In the range from 5 to 30 bar (entries 1−4), the rate (Figure 2d) increases with the H$_2$ pressure. Slowing occurs at ca. 10 bar, however. The highest conversion is observed at 30 bar. Above this pressure, the rate significantly decreases (ca. 23% at 70 bar) with no apparent change of selectivity (entries 6 and 7).

HPNMR Studies. When a MeOH-d_4 solution of **1** is pressurized with 30 bar of H$_2$ in a 10 mm HPNMR tube in the presence of a 10-fold excess of both BT and KOBu^t, no

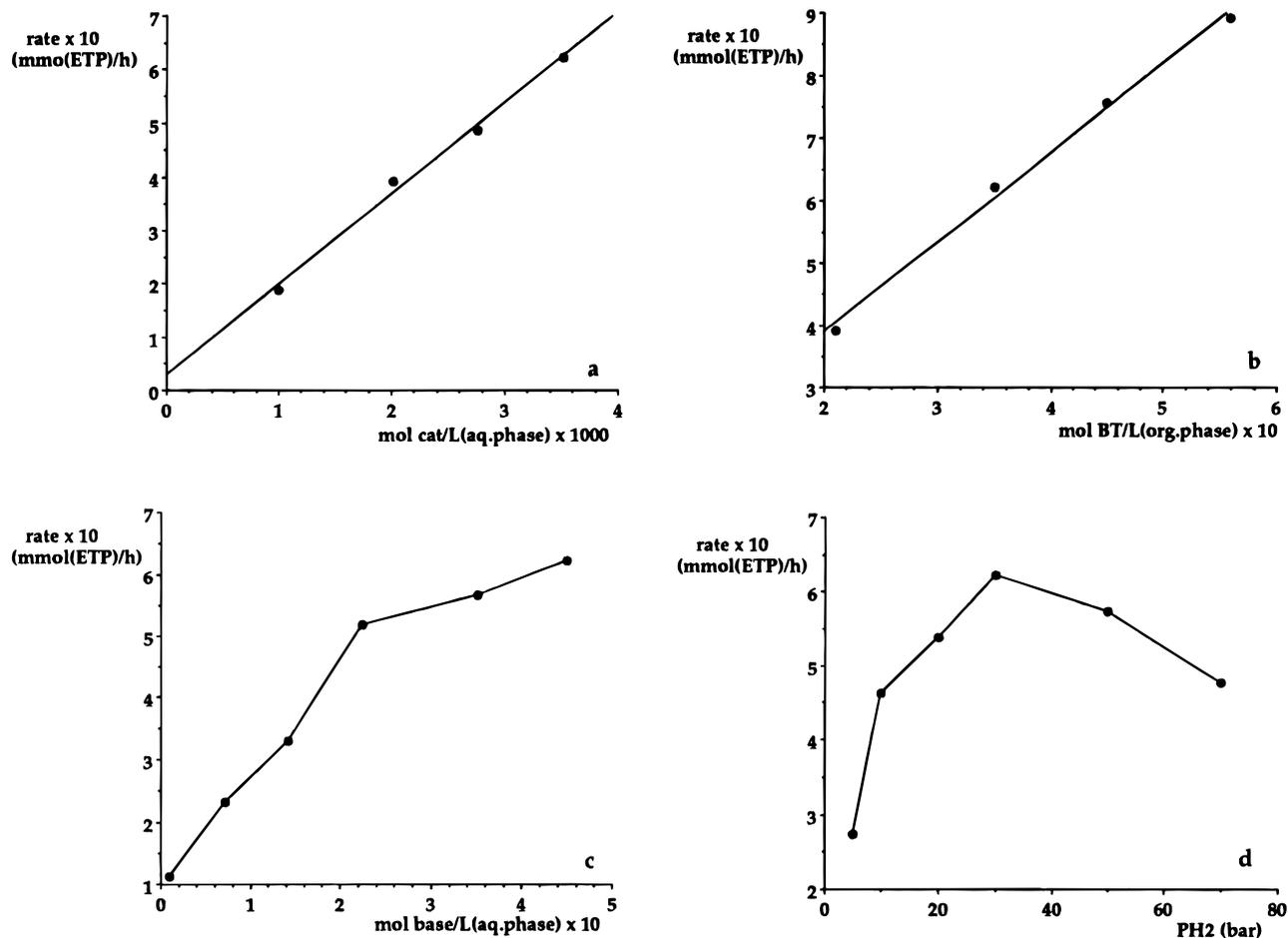(21) March, J. *Advanced Organic Chemistry,* 4th ed.; Wiley-Interscience: New York, 1992; pp 406−411.

Figure 2. Hydrogenolysis reactions of BT catalyzed by **1** at 160 °C. Dependence of the rate on the catalyst concentration (a), substrate concentration (b), base concentration (c), and hydrogen pressure (d).
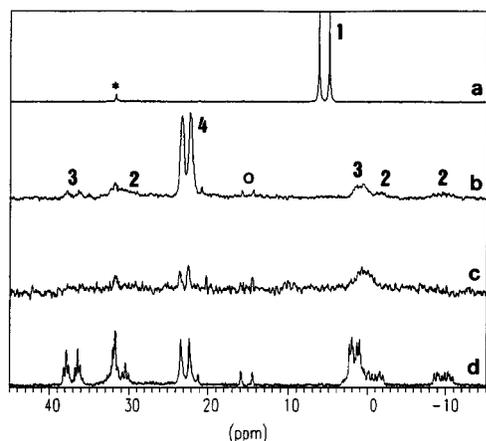

Figure 3. $^{31}P\{^1H\}$ HPNMR study (sapphire tube, MeOH-d_4, 81.01 MHz) of the catalytic hydrogenation of BT in the presence of **1** and KOBu^t (30 bar of H$_2$, BT:KOBu^t:**1** = 10:10:1). Spectrum at 20 °C (a), after the NMR probe was heated to 60 °C for 1.5 h (b) and to 120 °C for 2 h (c), and after the NMR probe was cooled to 20 °C (d). (*) Phosphine oxide. (○) Catalytically inactive, undefined species.

transformation of either **1** or BT is observed (on the NMR time scale) before a reaction temperature of ca. 60 °C is reached (Figure 3, trace a).

At 60 °C (trace b), all **1** is rapidly hydrogenated (formation of cyclooctene and cyclooctane) and the resulting metal fragment can react with either H$_2$ or BT or both. The reaction with H$_2$ gives a rhodium(III) trihydride product, [(sulphos)RhH$_3$]$^-$ (**4**) (^{31}P NMR A$_3$X pattern at 22.8 ppm), while the reaction with BT leads to the formation of the C−S insertion product

[(sulphos)Rh(η^3-S(C$_6$H$_4$)CH=CH$_2$)]$^-$ (**2**) (^{31}P NMR AMQX pattern with δ(P$_A$) 31.3, δ(P$_M$) −0.8, and δ(P$_Q$) −9.8). The concomitant action of H$_2$ and BT finally gives the 2-ethyl-thiophenolate complex [(sulphos)Rh(H)$_2$(o-S(C$_6$H$_4$)C$_2$H$_5$)]$^-$ (**3**) (^{31}P NMR AM$_2$X pattern with δ(P$_A$) 37.2 and δ(P$_M$) 1.8).
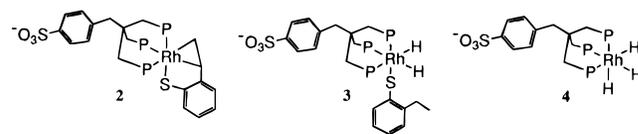
Traces of phosphine oxide (31.9 ppm) and of a fourth Rh species of undefined composition (A$_3$X pattern at 15.0 ppm) and with no active role in the conversion of BT (see below) are also detected.

At 60 °C for 1.5 h, no catalytic transformation of BT occurs as shown by ^{1}H NMR spectroscopy. Conversely, BT is catalytically hydrogenated to ETP (in the form of potassium 2-ethylthiophenolate salt) and DHBT as the temperature is increased to 120 °C. After 2 h at this temperature, a GC/MS analysis gave 47% conversion of BT to hydrogenolysis and hydrogenation products. At 120 °C under catalytic conditions, the only species visible on the NMR time scale are the trihydride **4** and the 2-ethylthiophenolate dihydride **3**, the latter product being formed in larger concentration than that of **4** (trace c). After the HPNMR reaction was quenched by decreasing the temperature of the probe head to 20 °C, a ^{31}P\{^{1}H\} NMR spectrum was acquired. The spectral resolution at 20 °C is sufficiently good to allow all coupling constants and the product ratios (**2**:**3**:**4** = 33:48:19) to be determined (trace d). In
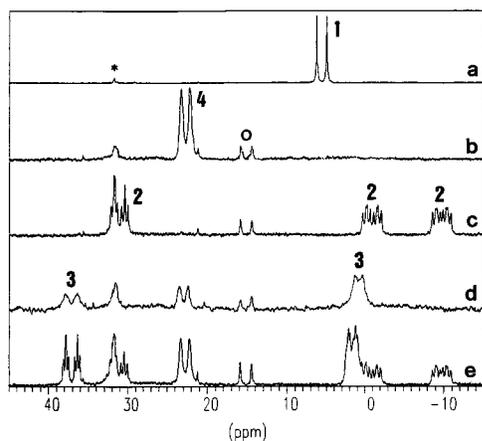
Figure 4. $^{31}P\{^1H\}$ HPNMR study (sapphire tube, MeOH-d_4, 81.01 MHz). Reaction of a 1:10 mixture of **1** and KOBu^t with 30 bar of H_2 [spectrum at 20 °C (a); spectrum recorded at 20 °C after 3 h of heating to 60 °C (b)]. Addition of a 10-fold excess of BT [spectrum recorded at 20 °C after 1 h of heating at 100 °C (c)]. Reaction of the resulting mixture with 30 bar of H_2 [spectrum recorded at 120 °C after 40 min (d); spectrum recorded after the NMR probe was cooled to 20 °C (e)]. (*) Phosphine oxide; (○) Catalytically inactive, undefined species.

comparison with the spectrum acquired at 120 °C (trace c), the spectrum at 20 °C shows that the dihydride complex **3** is still the major species but a large proportion of the 2-vinylthiophenolate product is also present. This means that **2** is formed during all the cooling time of the reaction mixture, while the reaction with H_2 to give **3** does not occur below ca. 60 °C. As already reported, this result is consistent with a lower energy barrier to C−S insertion as compared to the hydrogenation of the C−S inserted product.[9c,d,13]

A modeling study of independent reactions carried out in HPNMR tubes has provided conclusive evidence for the chemical relationships among **1**, **4**, **2**, and **3**, and between these compounds and the catalytic hydrogenolysis of BT. The results of this study are illustrated in Figure 4.

In the presence of a strong base, **1** in MeOH-d_4 (trace a) reacts with H_2 (30 bar) already at 60 °C to give the trihydride **4** (trace b). After the HPNMR tube was depressurized and all H_2 was replaced with N_2, a 10-fold excess of BT was introduced and the spectrometer probe head was heated to 100 °C for 1 h. As a result, the C−S bond cleavage of BT occurred with quantitative conversion of **4** to **2** (trace c) (following this procedure, **2** has been isolated as potassium salt **K2**). The tube was repressurized at room temperature with 30 bar of H_2 and then heated in the probe head. A reaction already occurred at 60 °C with transformation of the C−S insertion product **2** into both the 2-ethylthiophenolate dihydride **3** and the trihydride **4**. After 40 min at 120 °C (trace d), **3** and **4** were formed in a ca. 3 to 1 ratio. Consistent with the HPNMR study shown in Figure 3, when the probe head was slowly cooled to room temperature, the 2-vinylthiophenolate complex **2** reappeared (trace e).

The formation of some phosphine oxide in both HPNMR experiments is most likely due to the unavoidable introduction of traces of oxygen from air into the sapphire tube during charging and pressurizing operations. Likewise, one may not exclude that the byproduct at 15.0 ppm is formed by a side reaction with O_2. Whatever the origin of this compound may be, it is formed even in the absence of BT and reacts with neither BT nor its hydrogenation products. Any role of this species in the catalysis can thus be disregarded.

The formation of the trihydride **4** by treatment of **1** with H_2 does require the presence of a strong Brønsted base. As previously shown for the "(triphos)M" moieties (M = Rh, Ir;

triphos = MeC(CH$_2$PPh$_2$)$_3$),[9c,d,13,22] the base is needed to promote the heterolytic splitting of H_2 and ultimately generate *in situ* the [(sulphos)RhH]$^-$ fragment. The occurrence of a heterolytic splitting path accounts for the formation of a Rh complex with an odd number of hydride ligands (*i.e.*, **4**) in a reaction that involves the addition of H_2 to a Rh precursor devoid of a hydride ligand (*i.e.*, **1**). Accordingly, the strong base may be assigned a role as cocatalyst in the hydrogenolysis of BT assisted by **1**. In the absence of a base, **1** still reacts with H_2 (30 bar, 60 °C, HPNMR experiment) to give cyclooctane and a number of hydrido rhodium complexes which defied first-order analysis.

Although most of the sulphos products spectroscopically detected during the HPNMR experiments were not isolated in the solid state, their unambiguous identification is possible through a comparison of their NMR spectra with those of analogous Rh complexes with the triphos ligand. This differs from sulphos only in the group bonded to the bridgehead carbon atom (CH$_3$ vs CH$_2$(C$_6$H$_4$)SO$_3^-$). Indeed, it has already been found that the substitution of sulphos for triphos leads to insignificant variations of the ^{31}P NMR characteristics of corresponding compounds.[16] Thus, from a comparison of the NMR spectra of **4**, **2**, and **3** with those of authentic samples of [(triphos)Rh(H)$_3$] (**4***),[19] [(triphos)Rh(η^3-S(C$_6$H$_4$)CH=CH$_2$)] (**2***),[18] and [(triphos)Rh(H)$_2$(*o*-S(C$_6$H$_4$)C$_2$H$_5$)] (**3***),[9c] respectively, one may realize that, two by two, these compounds are essentially identical. On the other hand, this is quite reasonable as one is reminded how the triphos complexes are prepared: **2*** is synthesized by the thermolysis of the trihydride **4*** in the presence of BT,[18] and reacts with H_2 to give **3***.[9c] Moreover, both **2*** and **3*** have been found to play a role in the homogeneous hydrogenolysis of BT to ETP in THF: the former as a catalyst precursor, the latter as the major Rh complex during the catalysis and the Rh species that participates in the rate-determining step (*vide infra*).[9c,13]

Discussion

Hydrogenation and Hydrogenolysis of BT. In combination with a strong Brønsted base, the zwitterionic complex **1** reacts with H_2 to form an efficient catalyst for the hydrogenolysis of BT to ETP. The reactions can be carried out in pure MeOH or in biphasic systems comprising *n*-heptane as the organic phase and either MeOH or MeOH−H$_2$O as the polar phase. The catalyst system is thermally robust and can easily be recycled from the liquid-biphase reactions by phase separation. Small quantities of DHBT (1−4%) are also produced in the course of the reactions. As already reported for other related hydrogenolysis reactions of BT in the homogeneous phase,[9c,13] the production of DHBT is due to a side catalysis cycle (see below). Moreover, as shown by independent catalytic reactions, DHBT does not react with H_2 in the presence of the **1**/NaOH system; thus, any role of DHBT in the C−S bond scission reaction can be ruled out.[3−5]

MeOH is a necessary cosolvent in the biphase reactions because of the too low solubility of the catalyst precursor in pure H_2O. Since MeOH is a good solvent for BT, one may not exclude that the reactions in MeOH−H$_2$O/*n*-heptane may occur in the polar phase instead of taking place at the phase boundary as suggested for other ternary systems, *e.g.*, the hydrogenation of oct-1-ene in water/alcohol/oct-1-ene catalyzed by Rh/TPPMS.[23] On the other hand, **1**, like other sulphos

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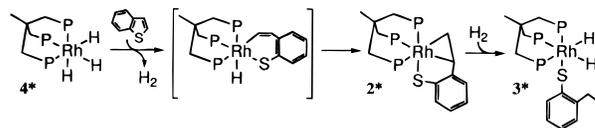
organometallic complexes, exhibits inherent surfactant properties that may lead to highly efficient emulsions.[14,16] Indeed, we have found that (i) irrespective of the phase system, comparable reactions proceed with essentially identical rate and selectivity, (ii) the addition of a surfactant does not increase the hydrogenolysis rate,[14,24] but a decrease eventually occurs, and (iii) the reactions do not need very high stirring rates to ensure rapid mass transfer. The hydrogenolysis rate of BT in MeOH−H$_2$O/ *n*-heptane is actually independent of the stirring rate in the 650−1800 rpm range. Accordingly, one can reasonably assume that the reaction rates are determined by the chemical aspects governing the catalytic process and not by the diffusion of the substrate between the aqueous and organic phases.

The exclusion of physical phenomena in determining the rate of conversion of BT is also suggested by the rate studies illustrated in Figure 2. As indicated in this Figure (a and b), the hydrogenolysis reaction is first-order with respect to the concentrations of the catalyst precursor and substrate. A linear correlation between the rate and the base concentration is also observed at initial NaOH concentrations lower than 0.224 M (NaOH to BT ratio of 0.6) (Figure 2c). At higher base concentrations, the rate almost levels off, most probably because of the too high ionic strength of the polar phase which may disfavor the mixing of the phases as well as the diffusion of BT.[14,25] Less intuitive is the dependence of the rate on the H$_2$ pressure illustrated in Figure 2d. The rate initially exhibits an increase, ultimately reaching a maximum at 30 bar, after which the rate decreases. A reasonable interpretation for this experimental observable may be forwarded in light of the HPNMR studies under catalytic conditions. These show that the proportion of the active catalyst, *i.e.*, the 16e$^-$ fragment [(sulphos)RhH]$^-$ (see below), sequestrated as the trihydride **4**, increases with pressure.
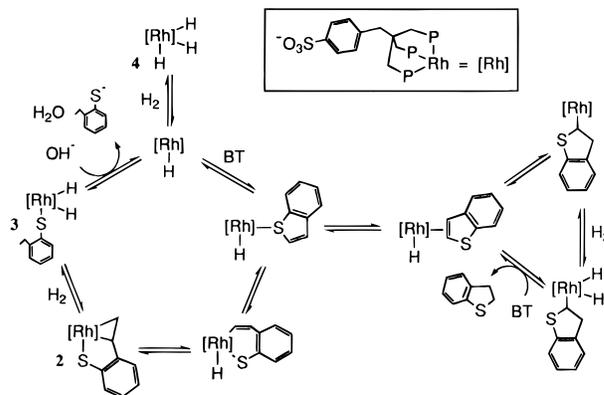
In the absence of a strong Brønsted base, **1** still reacts with H$_2$ to form a catalyst for the hydrogenation of BT. Irrespective of the phase variation, no opening of the thiophene ring occurs, however, whereas the C$_2$−C$_3$ double bond is selectively reduced to give DHBT. Due to the poor catalytic activity as well as the severe experimental conditions to achieve an appreciable production of DHBT, this hydrogenation reaction was not studied by HPNMR spectroscopy. A ^{31}P{^{1}H} NMR spectrum was acquired on a MeOH-d_4 solution of **1** pressurized with 30 bar of H$_2$. At 60 °C, all **1** disappeared to give several Rh complexes, none of which was identified by comparison with known triphos or sulphos complexes. Interestingly, the addition of KOBu^t to this mixture transformed part of the products into the trihydride **4**. This experiment further confirms that the strong base is necessary for the hydrogenolysis reaction to occur: the base deprotonates eventual rhodium(III) polyhydrido species (either classical or nonclassical) to give the rhodium(I) monohydrido fragment which brings about the C−S insertion step.[9d,13,24,26] On the other hand, the rate study illustrated in Figure 2c clearly shows that the role of the strong base cannot exclusively be that of generating the catalytically active species. It may be anticipated here that the base is of fundamental importance to facilitate the reductive elimination of the hydrogenolysis product from the metal center as commonly occurs in a variety of base-assisted reactions.

Mechanistic Conclusions. In earlier work, we have shown that the 16e$^-$ fragment [(triphos)RhH] is an efficient catalyst for the homogeneous hydrogenolysis of different thiophenes to the corresponding thiols in organic solvents such as THF or

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Scheme 3

Scheme 4

acetone (thiophene = thiophene, benzo[*b*]thiophene, dibenzo-[*b,d*]thiophene, and dinaphtho[2,1-*b*:1′,2′-*d*]thiophene).[9c,d,13] Irrespective of the thiophene, a general catalysis cycle has been proposed in which η^1-S coordination of the substrate is followed by insertion of Rh into a C−S bond. The resulting thiacycle is stepwise hydrogenated to give a dihydride thiolate complex that ultimately eliminates the thiol product, thus regenerating the [(triphos)RhH] catalyst.

Detailed mechanistic accounts for both the C−S insertion step and the hydrogenation of the resulting product have been given elsewhere.[9c,d,13,18,27] Here, it may be useful to recall briefly that the opening of BT proceeds by the regioselective insertion of the 16e$^-$ fragment [(triphos)RhH] into the C$_2$−S bond to give a metallathiacycle hydride intermediate. This rearranges to the 2-vinylthiophenolate complex **2*** by migration of the terminal hydride to the α-carbon atom of the vinyl moiety of the thiacycle (Scheme 3).[18,27] Both the C−S bond scission and the hydride migration reaction are low-energy processes occurring already at room temperature. Conversely, the hydrogenation of the C−S insertion product **2*** to the thiolate complex **3*** requires a high pressure of H$_2$ (> 15 bar) and a temperature higher than 60 °C.[9c]

As shown by the HPNMR studies (Figures 3 and 4), an analogous sequence of events occurs when sulphos is substituted for triphos. Accordingly, the catalysis cycle proposed for the hydrogenolysis of BT with [(triphos)RhH] can safely be extended to the reactions performed with [(sulphos)RhH]$^-$ (Scheme 4).[9c,13] A catalytic cycle of this type is also accounted for by the rate studies illustrated in Figure 2.

The reductive elimination of the thiol from the dihydride thiolate intermediate has been proposed to be the rate-determining step in the homogeneous hydrogenolysis of BT catalyzed by [(triphos)RhH] in aprotic organic solvents.[9c,13] This assumption can also be made for the reactions in polar media herein described on the basis of the HPNMR experiments as well as the rate studies, particularly the linear relationship between the hydrogenolysis rate and the base concentration.

A few further comments are to be noted. The biphase reactions are very selective, the production of DHBT being generally less than 2%. As already reported for triphos catalysis,[9c] the hydrogenation of BT to DHBT with monohydrido rhodium(I) species can proceed through a secondary cycle (right-

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Scheme 5
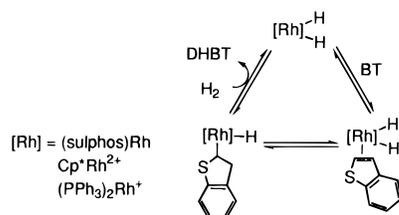
hand side of Scheme 4) in which the C_2-C_3 double bond of BT is hydrogenated through the general mechanism of olefin hydrogenation. In particular, the incorporation of deuterium in the unreacted BT seen in the HPNMR experiment in MeOH-d_4 is consistent with an equilibrium between the η^2-C,C-benzo-[b]thiophene hydride complex and its hydride-migration dihydrobenzothienyl product. The large prevalence of hydrogenolysis over hydrogenation can be attributed to steric effects[9c] as the η^1-S bonding mode of BT, precursor to C−S insertion,[5c,28] is less sterically demanding than the η^2-C,C one, precursor to double bond hydrogenation.[29]

The absence of a strong base in the catalytic mixture leads to a completely different activity and selectivity. A diverse mechanism is thus operative, which might well involve the standard sequence of steps already proposed by Fish[30] and Sánchez-Delgado[31] for the selective hydrogenation of BT to DHBT catalyzed by polyhydrido rhodium(III) complexes in the homogeneous phase (Scheme 5).

Conclusions

The data presented here define aqueous-biphase catalysis as a viable technique for the purification of petroleum distillates from residual thiophenic contaminants. Indeed, it has been shown that relevant reactions in the HDS of thiophenes such as the hydrogenolysis to thiols and the hydrogenation to thioethers can effectively be carried out in a liquid-biphase system with a metal complex exclusively soluble in the non-hydrocarbon phase and thus easily recycled. The introduction of the aqueous biphase technique to industrial HDS will require an enormous amount of research work to be carried out however. In particular, it will be necessary to design a class of water-soluble catalysts containing relatively inexpensive metals (Co, Ru) which are capable of tolerating the great thermal and chemical stress of the hydrotreatment and possibly endowed with inherent emulsifying attributes.

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