Mimicking the HDS Activity of Ruthenium-Based Catalysts. Homogeneous Hydrogenolysis of Benzo[*b*]thiophene

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Received February 6, 1998

The reaction of [(triphos)RuH(BH_4)] (**1**) in THF with KOBu^t yields the novel trihydride complex K[(triphos)RuH_3] (**2**) and BH_2OBu^t (triphos = $MeC(CH_2PPh_2)_3$). The ruthenate complex **2** can also be synthesized by hydrogenation (30 bar of H_2) in THF of the tris(acetonitrile) complex [(triphos)Ru$(NCMe)_3$]$(BPh_4)_2$ (**3**) in the presence of a 5-fold excess of BH_2OBu^t at 40 °C. This reaction produces a mixture of NH_2Et, $NHEt_2$, NEt_3, and NH_3 as a result of MeCN hydrogenation, followed by amine redistribution reactions. Compound **2** is isolated in analytically pure form as [K$(C_{12}H_{24}O_6)$][(triphos)RuH_3] (**2a**) by recrystallization from THF/*n*-hexane in the presence of 18-crown-6 ether. In the presence of a strong base such as KOBu^t, both **1** and **3** are effective catalyst precursors for the homogeneous hydrogenolysis of benzo[*b*]thiophene (BT) to 2-ethylthiophenol (ETP) in THF under mild reaction conditions (≥70 °C, 30 bar of H_2). The hydrogenolysis rate increases with the concentration of the base, which, depending on the catalyst precursor, may play up to three distinct roles in the catalytic reactions. It promotes the formation and stabilization of the catalytically active species (*i.e.* the 16e$^-$ fragment [(triphos)RuH]$^-$) and speeds up the hydrogenolysis rate, delivering the ETP product into the solution as 2-ethylthiophenolate potassium salt. High-pressure $^{31}P\{^1H\}$ and ^1H NMR experiments (HPNMR) in sapphire tubes sealed by titanium-alloy valves show that the interaction of **2** with BT at ≥70 °C in THF-d_8 selectively yields the dihydride thiolate complex K[(triphos)Ru$(H)_2$(*o*-$S(C_6H_4)C_2H_5$)] (**5**) under H_2 and the vinylthiophenolate complex K[(triphos)Ru(η^3-$S(C_6H_6)CH{=}CH_2$)] (**6**) under N_2. Compound **6** in THF transforms into **5** by treatment with H_2 even at room temperature. Under catalytic conditions at 70 °C, **5** and **2** are the only NMR-detectable species in equilibrium concentrations that depend on the temperature and on the base concentration. The hydrogenolysis mechanism is proposed to involve C−S insertion of ruthenium into the C_2−S bond of BT to give a 2-vinylthiophenolate ligand, followed by hydrogenation of the vinyl moiety and reductive elimination of the thiol. This latter step is accelerated by the strong Brønsted base. The possible similarity in the hydrogenolysis reactions catalyzed by the present soluble complexes to those occurring in the hydrodesulfurization of fossil fuels over Ru-promoted heterogeneous catalysts is discussed.

Introduction

Catalysts based on Co(Ni)−Mo sulfides supported on γ-Al_2O_3 have been used extensively over the last 50 years to remove sulfur from fossil fuel feedstocks *via* hydrodesulfurization (HDS) (eq 1).[1]

$$C_xH_yS + 2H_2 \xrightarrow{\text{cat.}} C_xH_{y+2} + H_2S \qquad (1)$$

The increasing demand for low-sulfur fuels and the need to process heavy oil supplies are precluding conventional catalysts, particularly with regard to the production of the so-called *city diesel*.[2] Catalysts comprising late transition metals such as platinum and palladium are definitely turning out to be most efficient for the *deep* HDS (<15 ppm sulfur) of naphthas after oil has been hydrotreated over Co(Ni)−Mo−S phases.[3] The high cost of the noble metals and the need to simplify the industrial process motivate the current research efforts aimed at developing a new generation of promoted Mo(W) catalysts.

Among the various approaches to rational catalyst design, modeling studies of the HDS chemistry of transition-metal compounds as either metal sulfides[1,4]

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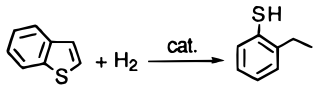
S0276-7333(98)00080-6 CCC: $15.00
Publication on Web 05/15/1998

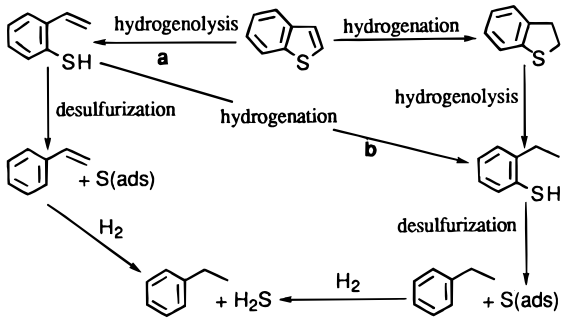
or organometallic complexes[5] point to ruthenium as one of the most active metals for the activation and/or degradation of the thiophenes, *i.e.* the sulfur compounds in petroleum which are the most difficult to desulfurize by hydrotreating. The optimistic picture provided by the model studies, however, contrasts with the fact that Ru-promoted catalysts are very rarely employed in refineries due to their quick deactivation. Similarly, the wealth, in number and variety of the stoichiometric transformations of thiophenes assisted by soluble ruthenium complexes[6] contrasts with the scarcity of homogeneous catalytic reactions.[5,7] We therefore decided to examine the catalytic activity of various ruthenium precursors in the hydrogenolysis and hydrogenation reactions of thiophenic molecules. To this end, we applied concepts and technologies previously and successfully developed for homogeneous rhodium and iridium catalysts.[8] In agreement with the heterogeneous studies, we were gratified to find that, under comparable conditions, ruthenium is catalytically more active than rhodium or iridium.

The present paper constitutes a detailed account of the first examples of homogeneous hydrogenolysis of benzo[*b*]thiophene (BT) to 2-ethylthiophenol (ETP) (eq 2) effectively catalyzed by ruthenium complexes.



(2)

Scheme 1



Reaction 2 involves C−S opening of BT, followed by hydrogenation of the C−S inserted product, and thus represents an important segment (steps a and b) of one of the paths through which the desulfurization of BT to ethylbenzene and H_2S is proposed to take place over heterogeneous HDS catalysts (Scheme 1).[1]

Experimental Section

General Information. All reactions and manipulations, except as stated otherwise, were routinely performed under a nitrogen atmosphere by using standard Schlenk techniques. Reactions under controlled pressure of hydrogen were performed with a stainless steel Parr 4565 reactor equipped with a Parr 4842 temperature and pressure controller. The ruthenium complex [(triphos)Ru(H)BH_4 (**1**) was prepared as previously described.[9] The complex [(triphos)Ru$(NCMe)_3$]$(BPh_4)_2$ (**3**) was prepared from the known compound [(triphos)Ru$(NCMe)_3$]$(SO_3CF_3)_2$[10] by a metathetical reaction with $NaBPh_4$ in McCN/ethanol. All the isolated metal complexes were collected on sintered-glass frits and washed with appropriate solvents before being dried under a stream of nitrogen. Tetrahydrofuran (THF) and THF-d_8 were purified by distillation under nitrogen from $LiAlH_4$. MeCN was distilled from CaH_2. Benzo[*b*]thiophene (99%, Aldrich) was sublimed prior to use. Potassium *tert*-butoxide ($KOBu^t$, 95%), 18-crown-6 ether (99.5%), $LiHBEt_3$ (1.0 M solution in THF), 2-ethylthiophenol (90%), and polyvinylpyrrolidone K25 (average M_w 29 000, PVP) were purchased from Aldrich and used without further purification. 2,3-Dihydrobenzo[*b*]thiophene (DHBT) was prepared by catalytic hydrogenation of BT assisted by **3**.[11] All the other reagents and chemicals were reagent grade and were used as received from commerical suppliers. ^1H (200.13 MHz) and $^{31}P\{^1H\}$ (80.01 MHz) NMR spectra were obtained on a Bruker ACP 200 spectrometer. All chemical shifts are reported in ppm (δ) relative to tetramethylsilane, referenced to the chemical shifts of residual solvent resonances (^1H) 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 the ISSECC-CNR (Firenze, Ital).[12] *Note! Since high gas pressures are involved, safety precautions must be taken at all stages of studies involving high-pressure NMR tubes.* The computer simulation of NMR spectra was carried out with a locally developed package containing the programs LAOCN3[13] and Davins.[14] The initial choices of shifts and coupling constants were refined by iterative least-squares calculations using

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experimental digitized spectra. The final parameters gave a satisfactory fit between experimental and calculated spectra, the agreement factor R being less than 1% in all cases. 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 with a column identical with that used for GC analyses. Infrared spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrophotometer using samples mulled in Nujol between KBr plates. 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.

Synthesis of K[(triphos)RuH$_3$] (2). Solid KOBu^t (85 mg, 0.72 mmol) was added to a stirred suspension of [(triphos)-Ru(H)BH$_4$] (**1**; 180 mg, 0.24 mmol) in THF (20 mL) at room temperature. After 30 min the resulting yellow-orange solution was pumped to dryness and the beige solid residue was washed with *n*-pentane. NMR analysis of this product showed the formation of a unique Ru−triphos complex with the following spectral features. ^{31}P{^{1}H} NMR (THF-d_8, 20 °C): A_3 spin system, δ 44.1 (s). ^{1}H NMR (THF-d_8, 20 °C): δ 2.09 (d, 6H, J(HP) = 5.3 Hz, CH_2P), 1.39 (q, 3H, J(HP) = 2.2 Hz, CH_3), −7.73 (AA′A″XX′X″ spin system, second-order doublet of multiplets, 3H, $|J(HP_{trans}) + 2J(HP_{cis})|$ = 43.1 Hz, Ru−H). All our attempts to recrystallize **2** from organic solvents to eliminate the KOBu^t impurity led to extensive decomposition. Only when crude **2** was dissolved in THF containing a slight excess of 18-crown-6 ether did the addition of *n*-heptane lead to the precipitation of pure [K(C$_{12}$H$_{24}$O$_6$)][(triphos)RuH$_3$] (**2a**) in 65% yield. Anal. Calcd (found) for C$_{53}$H$_{66}$KO$_6$P$_3$Ru: C, 61.67 (61.09); H, 6.45 (6.38); Ru, 9.79 (9.54). ^{31}P{^{1}H} NMR (THF-d_8, 20 °C): A_3 spin system, δ 44.1 (s). ^{1}H NMR (THF-d_8, 20 °C): δ 2.20 (d, 6H, J(HP) = 5.3 Hz, CH_2P), 1.50 (q, 3H, J(HP) = 2.1 Hz, CH_3), −7.28 (AA′A″XX′X″ spin system, second-order doublet of multiplets, 3H, $|J(HP_{trans}) + 2J(HP_{cis})|$ = 46.9 Hz, Ru−H). IR: ν(Ru−H) 1850 (m), 1828 (m) cm^{-1}. Compounds **2** and **2a** are stable in both the solid state and dry THF solution under a dry nitrogen or hydrogen atmosphere; both compounds are extremely sensitive to moisture as well as any sort of Brønsted and Lewis acids.

Reaction of [(triphos)Ru(NCMe)$_3$](BPh$_4$)$_2$ (3) with H$_2$ in the Presence of KOBu^t. Sapphire Tube HPNMR Experiment. A 10 mm sapphire HPNMR tube was charged with a solution of **3** (36 mg, 0.024 mmol) and a 10-fold excess of KOBu^t (28 mg, 0.24 mmol) in THF-d_8 (2 mL) under nitrogen. The tube was pressurized with hydrogen to 30 bar at room temperature and then placed into a NMR probe. The reaction was followed by variable-temperature ^{31}P{^{1}H} and ^{1}H NMR spectroscopy. The transformation of the starting tris(acetonitrile) complex **3** occurred even at room temperature, yielding [(triphos)Ru(H)(NCMe)$_2$]BPh$_4$ (**4**; see below) and other unidentified minor species (1 h). Increasing the temperature to 40 °C led to the gradual conversion of all the previously formed compounds to the ruthenate complex **2** (3 h). After the NMR probe was cooled to room temperature, **2** was the only metal product visible by ^{31}P{^{1}H} NMR spectroscopy. The tube was then removed from the spectrometer and cooled to −20 °C and the gas phase was analyzed by GC, showing the presence of NH$_3$. The cool liquid contents of the tube were then transferred into a Schlenk-type flask maintained at −20 °C. GC and GC/MS analysis of the solution showed the formation of NH$_2$Et, NHEt$_2$, and NEt$_3$ in a ratio of 11:4:1. Further NH$_3$ was also detected.

Synthesis of [(triphos)Ru(H)(NCMe)$_2$]BPh$_4$ (4). To a solution of **3** (150 mg, 0.1 mmol) in MeCN (5 mL) was added a 4-fold excess of LiHBEt$_3$ (0.4 mL, 0.4 mmol). After 10 min, addition of ethanol (5 mL) and *n*-heptane (60 mL) led to the precipitation of **4** as pale yellow microcrystals in 80% yield. Anal. Calcd (found) for C$_{69}$H$_{66}$BN$_2$P$_3$Ru: C, 73.46 (73.12); H, 5.90 (5.80); N, 2.48 (2.31); Ru, 8.96 (8.77). ^{31}P{^{1}H} NMR (THF-d_8, 20 °C): AM_2 spin system, δ 48.2 (d, $J(P_MP_A)$ = 20.8 Hz, P_M), 6.5 (t, P_A). ^{1}H NMR (THF-d_8, 20 °C): δ 2.8−2.3 (m, 6H, CH_2P), 1.71 (q, 3H, J(HP) = 2.3 Hz, CH_3), 1.62 (d, 6H, J(HP) = 1.4 Hz, *Me*CN), −5.16 (dt, 1H, $J(HP_A)$ = 105.3 Hz, $J(HP_M)$ = 19.3 Hz, Ru−H). IR: ν(Ru−H) 1850 (s) cm^{-1}.

Reaction of K[(triphos)RuH$_3$] (2) with BT. A. HPNMR Experiment under Hydrogen. A 10 mm HPNMR tube was charged under nitrogen first with a solid sample of **1** (18 mg, 0.024 mmol) together with a 3-fold excess of solid KOBu^t (9 mg, 0.072 mmol) and then with a THF-d_8 (2 mL) solution containing a 5-fold excess of BT (16 mg, 0.12 mmol). The tube was pressurized with hydrogen to 3 bar at room temperature and then placed into a NMR probe at room temperature. The reaction was monitored by ^{31}P{^{1}H} and ^{1}H NMR spectroscopy. Within 1 h, **1** completely disappeared; formed in its place was **2**. The temperature of the NMR probe was then increased gradually to 50 and 70 °C. Only at the latter temperature did a fast reaction occur, which converted all of **2** to the dihydride thiolate ruthenate complex K[(triphos)Ru(H)$_2$(*o*-S(C$_6$H$_4$)C$_2$H$_5$)] (**5**) in ca. 30 min. After the NMR probe was cooled to room temperature, **5** was the only metal product visible by NMR spectroscopy with the following spectral features. ^{31}P{^{1}H} NMR: AM_2 spin system, δ 57.2 (t, $J(P_AP_M)$ = 24.1 Hz, P_A), 25.1 (d, P_M). ^{1}H NMR: δ 2.94 (q, 2H, J(HH) = 7.5 Hz, CH_2CH$_3$), 2.6−2.1 (m, 6H, CH_2P), 1.48 (q, 3H, J(HP) = 2.2 Hz, CH_3), 1.23 (t, 3H, CH$_2$CH_3), −6.88 (AA′XX′Y spin system, second-order doublet of multiplets, 2H, $J(H_AH_{A'})$ = 9.45 Hz, $J(H_AP_X)$ = 85.44 Hz. $J(H_AP_{X'})$ = −11.56 Hz, $J(HP_Y)$ = 23.81 Hz, $J(P_XP_{X'})$ = −17.22 Hz, Ru−H).

B. HPNMR Experiment under Nitrogen. A 10 mm HPNMR tube was charged under nitrogen first with a solid sample of **1** (18 mg, 0.024 mmol) together with a 3-fold excess of solid KOBu^t (9 mg, 0.072 mmol) and then with a THF-d_8 (2 mL) solution containing a 5-fold excess of BT (16 mg, 0.12 mmol). The reaction was monitored by variable-temperature ^{31}P{^{1}H} and ^{1}H NMR spectroscopy. A sequence of selected ^{31}P-{^{1}H} NMR spectra is reported in Figure 1. Within 1 h, **1** completely converted into **2** (trace a). The temperature of the NMR probe was then increased to 100 °C. The ^{31}P{^{1}H} NMR spectra acquired during the following 3 h showed the gradual disappearance of **2**; formed in its place was a broad resonance centered at ca. 24 ppm which was assigned (see below) to the fluxional vinylthiophenolate complex K[(triphos)Ru(η^3-S(C$_6$H$_4$)-CH=CH$_2$)] (**6**; trace b). The slow-exchange regime of the latter complex was attained at room temperature, where **6** was the only metal product visible in the reaction mixture by NMR spectroscopy with the following spectral features (trace c). ^{31}P-{^{1}H} NMR: AMQ spin system, δ 47.3 (t, $J(P_AP_M)$ = 33.1 Hz, $J(P_AP_Q)$ = 28.1 Hz, P_A), 25.5 (dd, $J(P_MP_Q)$ = 13.1 Hz, P_M), 12.7 (dd, P_Q). ^{1}H NMR: δ 2.79 (m, CH=CH$_2$), 2.3 (masked by aliphatic resonances of triphos, CH=CHH'), 1.7 (masked by THF, CH=CHH′). The tube was pressurized with hydrogen to 30 bar at room temperature and then placed into a NMR probe. The ^{31}P{^{1}H} NMR spectra of this sample, recorded at room temperature over the following 2 h, showed the gradual conversion of **6** into **5** (trace d, after 2 h). Complete conversion of **6** into **5** was achieved by increasing the temperature to 40 °C; a small amount of the trihydride **2** was also detected. The reaction between **2** and BT, although slow, occurred even at 70 °C with the same sequence of products.

All our attempts to isolate **6** from batch reactions were unsuccessful. Every treatment of the reaction mixture invariably led to the decomposition of **6** to several unidentified products.

Reactions of K[(triphos)RuH$_3$] (2) with ETP. A. NMR Experiment. A Teflon-capped resealable 5 mm NMR tube was charged first with a solid sample of **1** (18 mg, 0.024 mmol) together with a 3-fold excess of solid KOBu^t (9 mg, 0.072 mmol) and then with THF-d_8 (1 mL) under nitrogen. The tube was

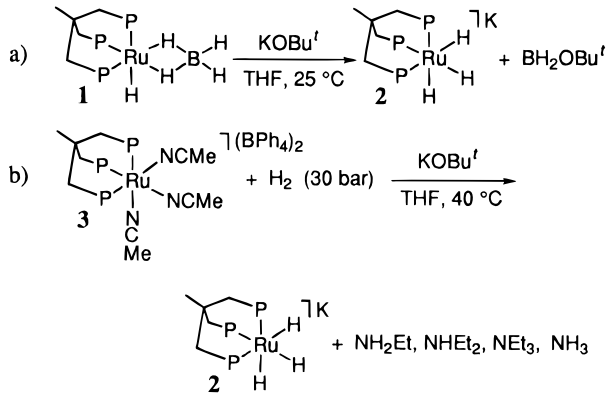
placed into a NMR probe at room temperature. The reaction was monitored by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. Within 1 h, compound **1** converted to **2**. Afterward, 1 equiv of ETP was syringed into the tube at room temperature. The $^{31}P\{^1H\}$ and ^1H NMR spectra of this sample showed the complete conversion of **2** to **5** and H_2 (^1H NMR singlet at δ 4.7).

B. Synthetic Experiment. A suspension of **1** (180 mg, 0.24 mmol) together with a 3-fold excess of solid KOBu^t (85 mg, 0.72 mmol) in THF (20 mL) was stirred at room temperature. After ca. 30 min, 1 equiv of ETP was syringed into the solution. After 10 min, a 0.5 mL portion of this solution was withdrawn and diluted with 0.5 mL of THF-d_8 for the $^{31}P\{^1H\}$ and ^1H NMR analysis. Compound **5** was the only ruthenium complex detected in solution on the NMR time scale. All our attempts to isolate **5** from this solution were unsuccessful. Attempted isolation of **5** by either precipitation with various solvents under a nitrogen or dihydrogen atmosphere or concentration of the reaction mixture to dryness under vacuum invariably led to the decomposition of the desired complex to several unidentified products. Solutions of **5** in THF are extremely sensitive to air and acids.

Reaction of K[(triphos)Ru(H)$_2$(*o*-S(C$_6$H$_4$)C$_2$H$_5$)] (5) with H$_2$ (30 bar) in the Presence of Excess K[*o*-S(C$_6$H$_4$)C$_2$H$_5$]. HPNMR Experiment. ETP (5 equiv) was syringed into a 10 mm sapphire HPNMR tube containing a solution of **2** (prepared by reacting **1** (18 mg, 0.024 mmol) with a 10-fold excess of KOBu^t (28 mg, 0.24 mmol) in THF-d_8 (2 mL) under nitrogen). The tube was placed into a NMR probe at room temperature and heated to 70 °C. After ca. 1 h, the $^{31}P\{^1H\}$ and ^1H NMR spectra of this sample showed the complete conversion of **2** to **5**. At this point, the tube was cooled to room temperature and pressurized with hydrogen to 30 atm; then it was placed into the NMR probe again and heated to 70 °C. Even the first $^{31}P\{^1H\}$ NMR spectrum showed the characteristic resonances of **2**. Spectra acquired after 1 and 2 h were practically identical with each other, showing a **2**:**5** ratio of ca. 10. No other signal was visible by NMR. After the tube was cooled to room temperature, **2** and **5** were still the only detectable metal products. The tube was depressurized in order to add further KOBu^t (0.24 mmol). After the tube was repressurized to 30 bar of H_2, it was introduced into the probe head and heated to 70 °C. Under these conditions, the concentration of the trihybride **2** increased remarkably at the expense of that of **5** (**2**:**5** ratio of 50) as a result of the delivery of the thiolate ligand into the solution as the potassium salt.

Hydrogenolysis of BT of 2-Ethylthiophenolate. 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 either the tetrahydroborate complex **1** (32 mg, 0.043 mmol) or the tris(acetonitrile) derivative **3** (65 mg, 0.043 mmol) in THF (30 mL) and 100-fold excesses of both BT (579 mg, 4.3 mmol) and KOBu^t (510 mg, 4.3 mmol) were placed into the Parr reactor under a nitrogen atmosphere. After pressurizing with hydrogen to 30 bar at room temperature, the mixture was heated to the appropriate temperature and then immediately stirred (750 rpm). After the desired time, the reactor was cooled to room temperature and slowly depressurized. The contents of the reactor were transferred into a Schlenk-type flask and acidified with aqueous HCl to ca. pH 5 to convert 2-ethylthiophenolate sodium salt to 2-ethylthiphenol (ETP).[8a] 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.[8a] A sample of the solution was withdrawn and analyzed by GC and GC/MS. Several catalytic reactions were carried out in the presence of excess elemental Hg (2000:1) to test the homogeneous character of the reactions. In all cases, no change in both activity and chemoselectivity was observed. Similarly, the catalytic activity did not significantly change when the reactions were carried out in the presence of variable amounts of a colloid-protecting agent such as polyvinylpyrrolidone (PVP) from 0.1 to 100% with respect to the catalyst precursor).

Scheme 2



B. Sapphire Tube HPNMR Experiment with the Catalyst Precursor [(triphos)Ru(H)BH$_4$] (1). A 10 mm sapphire HPNMR tube was charged first with solid samples of **1** (18 mg, 0.024 mmol) and KOBu^t (28 mg, 0.24 mmol) and then with a solution containing a 30-fold excess of BT (96 mg, 0.72 mmol) in THF-d_8 (2 mL) under nitrogen. The tube was pressurized with hydrogen to 30 bar at room temperature and then placed into a NMR probe at 20 °C. The reaction was followed by variable-temperature $^{31}P\{^1H\}$ and ^1H NMR spectroscopy in the range 20−70 °C. The results of this study are described in detail in a forthcoming section and illustrated in Figure 2. After ca. 4 h at 70 °C, the tube was removed from the spectrometer and depressurized to ambient pressure. the $^{31}P\{^1H\}$ NMR spectrum was identical with that of a pure sample of **5**. 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 (18%), BT (82%), and DHBT (<1%).

When isolated **2** was employed instead of **1**, the reaction followed an identical path.

C. Sapphire Tube HPNMR Experiment with the Catalyst Precursor [(triphos)Ru(NCMe)$_3$](BPh$_4$)$_2$ (3). A 10 mm sapphire HPNMR tube was charged with a solution of **3** (36 mg, 0.024 mmol), a 10-fold excess of KOBu^t (28 mg, 0.24 mmol), and a 30-fold excess of BT (96 mg, 0.72 mol) in THF-d_8 (2 mL) under nitrogen. The tube was pressurized with hydrogen to 30 bar at room temperature and then placed into a NMR probe at 20 °C. The reaction was followed by variable-temperature $^{31}P\{^1H\}$ and ^1H NMR spectroscopy in the temperature range 20−70 °C for an overall time of ca. 4 h. The results of this study are described in detail in a forthcoming section and illustrated in Figure 3. After the catalytic reaction was quenched by cooling to room temperature, **5** was the only metal product visible by $^{31}P\{^1H\}$ NMR spectroscopy. After the tube was depressurized, its contents were transferred into a Schlenk-type flask. A portion of this solution, after acidification with HCl(aq), was analyzed by GC and GC/MS: ETP (11%), BT (84%), and DHBT (5%). GC and GC/MS analysis of the rest of the solution led to the identification of NH_2Et, $NHEt_2$, and NEt_3 in a ratio of ca. 9:3:1.

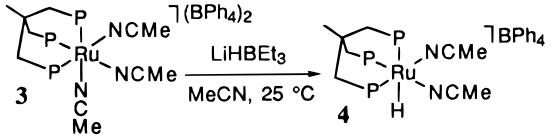
Results and Discussion

Synthesis and Characterization of the Catalyst Precursor K[(triphos)RuH$_3$]. The novel Ru(II) trihydride complex K[(triphos)RuH$_3$] (**2**) is quantitatively formed upon treatment of [(triphos)RuH(BH$_4$)][9] (**1**) in THF with a 3-fold excess of KOBu^t at room temperature (Scheme 2a). The elimination of the BH_2 moiety from **1** by reaction with Lewis bases is a known process, previously employed by Venanzi to generate *in situ*

heteropolymetallic complexes with bridging hydride ligands.[15] The mononuclear compound **2** is isolated in the solid state as a beige powder by solvent elimination under reduced pressure. Once isolated, **2** can be handled and weighed safely under a dry nitrogen atmosphere to prepare solutions in anhydrous THF. The compound is extremely sensitive to moisture and protic solvents (*vide infra*); in the presence of a slight excess of $KOBu^t$, however, THF solutions of **2** do not show appreciable decomposition for days, given the rigorous absence of water. All our attempts to recrystallize **2** from organic solvents resulted in its extensive decomposition unless a crown ether such as 18-crown-6 ether was added. In this case, the complex $[K(C_{12}H_{24}O_6)][triphos)RuH_3]$ (**2a**) was obtained in fairly good yields from THF/*n*-heptane.

An alternative, very efficient synthesis of **2** in THF solution is provided by the hydrogenation (30 bar of H_2) of the tris(acetonitrile) complex $[(triphos)Ru(MeCN)_3](BPh_4)_2$ (**3**) at 40 °C in the presence of a 10-fold excess of $KOBu^t$ (Scheme 2b). Water must be rigorously eliminated from the reaction mixture to avoid the irreversible formation of the dimer $[(triphos)Ru(\mu\text{-}OH)_3Ru(triphos)]BPh_4$ (**7**).[16]

The reaction between **3** and H_2 in the presence of $KOBu^t$ was followed by NMR spectroscopy in a high-pressure sapphire tube sealed with a Ti-alloy valve. As shown by an *in situ* HPNMR experiment at 40 °C, the formation of **2** is preceded by that of several ruthenium complexes, among which only the hydride complex $[(triphos)RuH(MeCN)_2]BPh_4$ (**4**) was unambiguously identified by its independent synthesis from **3** and $LiHBEt_3$ in MeCN (eq 3). All the other ruthenium



(3)

complexes have a fleeting existence and are rapidly converted to **2**.

After all **3** has been converted to **2**, no trace of MeCN is detected in solution by GC. Formed in its place the mixtures of NH_2Et, $NHEt_2$, NEt_3, and NH_3. These amines are most likely produced upon hydrogenation of MeCN to the primary amine (*via* an imine intermediate), followed by amine redistribution reactions which first give the secondary amine and ammonia and then the tertiary amine and further ammonia.[17] As expected, the NH_2Et:$NHEt_2$:NEt_3 ratios decrease with the temperature, while the concentration of NH_3 increases. In an *in situ* experiment at 40 °C for 3 h, a 11:4:1 ratio between NH_2Et, $NHEt_2$, and NEt_3 was determined by GC/MS. The overall transformation pattern undergone by the acetonitrile ligands in **3** is well-known for Ru-catalyzed homogeneous hydrogenations of nitriles and has been suggested to proceed *via* the reaction sequence summarized in eq 4.[17a]

$$\begin{aligned} &RCN \xrightarrow{H_2} RCH{=}NH \xrightarrow{H_2} RCH_2NH_2 \xrightarrow{RCN} \\ &RCH_2NHC(R){=}NH \xrightarrow{H_2} RCH_2NHCH(R)NH_2 \xrightarrow{-NH_3} \\ &RCH_2N{=}CHR \xrightarrow{H_2} (RCH_2)_2NH \xrightarrow{RCN} \xrightarrow{H_2} \xrightarrow{-NH_3} \xrightarrow{H_2} \\ &(RCH_2)_3N \end{aligned} \quad (4)$$

The fact that the first metal product to form is the monohydrido complex **4** is a clear indication that a heterolytic splitting of H_2 assisted by the strong base occurs initially at the metal center. Most likely, it is a Ru(II) hydride complex, similar to **4**, the species which catalyzes the acetonitrile hydrogenation/amine redistribution reactions, in the course or at the end of which **2** is formed upon two further heterolytic splittings of H_2.

Compound **2** belongs to a relatively numerous family of *fac* triphosphine trihydride metal complexes, among which $[(triphos)RhH_3]$ and $[(triphos)IrH_3]$ are those sharing with **2** the greatest number of structural and spectroscopic analogies.[18] As for the Rh and Ir derivatives, the $^{31}P\{^1H\}$ NMR spectrum of **2** consists of a temperature-invariant A_3 spin system, while the three chemically but not magnetically equivalent hydride ligands give rise to a highly perturbed AA′A″XX′X″ pattern. From a chemical viewpoint, however, the closest parent of **2** is the ruthenate $K[fac\text{-}RuH_3(PPh_3)_3]$.[19] Indeed, like the PPh_3 analog, **2** reacts with proton donors of different strength (water, alcohols, protic acids), yielding equilibrium concentrations of the tetrahydrido complex $[(triphos)RuH_4]$ (**8**).[16] In the absence of a positive H_2 pressure, the latter complex is not stable in solution, where it readily forms the $16e^-$ Ru(II) fragment $[(triphos)Ru(H)_2]$, which either dimerizes to give the red complex $[(triphos)RuH(\mu\text{-}H)_2HRu(triphos)]$ (**9**) or is intercepted by nucleophiles to give mononuclear adducts. For example, the novel dihydride $[(triphos)Ru(H)_2(CO)]$ (**10**) is quantitatively obtained by bubbling CO into a THF/ethanol solution of **2**.[16] Details of these transformations are not given here, as the reactions which are of peculiar interest to this work are just those with either BT or ETP.

Reactions of K[(triphos)RuH$_3$] with Benzo[*b*]thiophene or 2-Ethylthiophenol. NMR shows that **2** in THF is capable of cleaving BT, yielding the vinylthiophenolate complex $K[(triphos)Ru(\eta^3\text{-}S(C_6H_4)CH{=}CH_2)]$ (**6**) even at 70 °C. At the same temperature but in the presence of a positive pressure of H_2, the dihydride 2-ethylthiophenolate complex $K[(triphos)Ru(H)_2(o\text{-}S(C_6H_4)C_2H_5)]$ (**5**) is quantitatively obtained (Scheme 3a,b; Figure 1). Since **6** is a precursor to **5** *via* hydrogenation, the overall hydrogenolysis of BT definitely proceeds *via* C−S insertion/hydrogenation and not by the alternative hydrogenation/C−S insertion seqeuence.[1,5] Consistently, the hydrogenated product 2,3-dihydrobenzo[*b*]thiophene (DHBT) does not react with **2** under identical reaction conditions.

(15) Albinati, A.; Venanzi, L. M.; Wang, G. *Inorg. Chem.* **1993**, *32*, 3660.

(16) A detailed account of the reactivity of **2** toward proton donors alone or in combination with nucleophiles or strong bases will be given elsewhere. This kind of information is not relevant to the main subject of this work. Spectral and analytical data for compounds **7**−**10** are given as Supporting Information.

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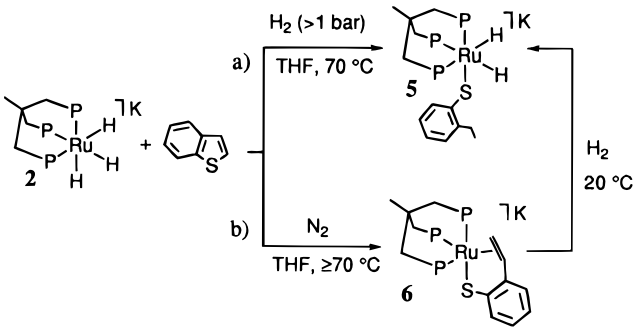
(19) Linn, D. E., Jr.; Halpern, J. *J. Am. Chem. Soc.* **1987**, *109*, 2969.

Scheme 3



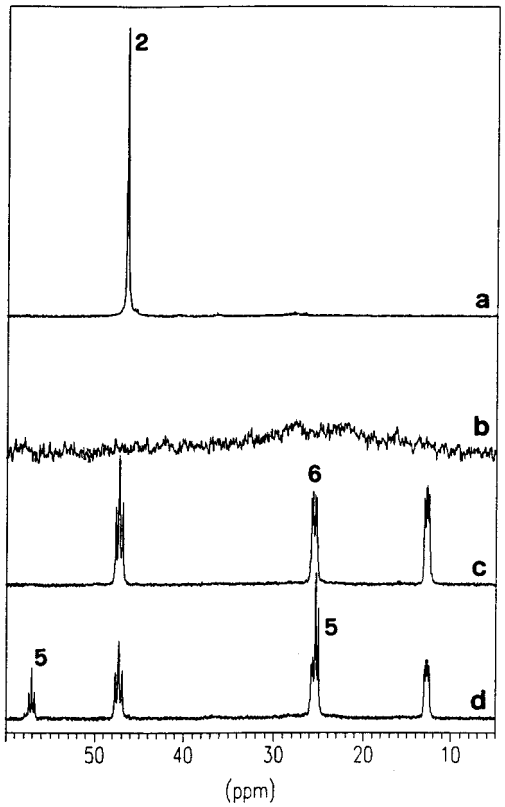


Figure 1. $^{31}P\{^1H\}$ NMR study (sapphire tube, THF-d_8, 81.01 MHz) of the reaction of **2** with BT: (a) at room temperature under nitrogen; (b) at 100 °C after 3 h; (c) after the tube was cooled to room temperature; (d) at room temperature after the tube was pressurized with 30 bar of H_2 for 2 h.

Compound **5** has been identified by NMR spectroscopy as well as its independent preparation by the reaction of **2** in THF with pure ETP (Scheme 3b). In particular, the AM_2 pattern of the phosphorus nuclei and the AA′XX′Y (X, Y, = P) pattern of the two terminal hydrides are quite comparable to those of the congeners [(triphos)M(H)$_2$(*o*-S(C$_6$H$_4$)C$_2$H$_5$)] (M = Rh, Ir) similarly prepared by C−S insertion/hydrogenation of BT (Scheme 4).[8d,20]

Like the rhodium analog [(triphos)Rh(H)$_2$(*o*-S(C$_6$H$_4$)-C$_2$H$_5$)],[8d] **5** is thermally unstable in solution, losing H_2 even at room temperature unless a protective atmosphere of this gas is employed. As the H_2 pressure is increased to 30 bar, however, **5** partially reconverts to **2** through the elimination of ETP (Scheme 3b). HPNMR also shows that, under 30 bar of H_2, the equilibrium (5) is shifted to the right by addition of increasing amounts of KOBu^t.

$$[(\text{triphos})\text{Rh}(\text{H})_2(o\text{-S}(\text{C}_6\text{H}_4)\text{C}_2\text{H}_5)]^- + \text{H}_2 + \text{Bu}^t\text{O}^- \rightleftarrows [(\text{triphos})\text{RuH}_3]^- + [o\text{-S}(\text{C}_6\text{H}_4)\text{C}_2\text{H}_5]^- + \text{Bu}^t\text{OH} \quad (5)$$

Unlike **5**, we were unable to independently prepare **6**. The identification of this C−S insertion product was therefore based on its spectroscopic characteristics, which are quite similar to those of the related Rh(I) and Ir(I) 2-vinylthiophenolate neutral complexes [(triphos)M(η^3-S(C$_6$H$_4$)CH=CH$_2$)] (M = Ir,[20] Rh) (see Scheme 4).[21d] In particular, the ^{31}P NMR spectrum shows a canonical AMQ pattern, while signals at 2.79 (CH_2) and 2.3 and 1.7 ppm (CHH′) in the ^1H NMR spectrum can safely be attributed to a vinyl group bound to ruthenium.[20,21d] Further support tothe proposed structure for **6** is provided by its quantitative conversion to **5** by treatment with H_2.

Due to the availability of filled metal dπ orbitals of appropriate energy and symmetry to interact withthe π^* C$_2$−S orbital,[5] the cleavage of the C$_2$−S bond of BT by 16e$^-$ metal fragments of the type [(triphos)MH] (M = Rh, Ir) is a low-energy process indeed.[8,20,21] In particular, it is lower in energy than the thermal processes which are necessary to generate the 16e$^-$ fragments from their 18e$^-$ precursors (see Scheme 4). The Ru(0) system [(triphos)RuH]$^-$, generated by reductive elimination of H_2 from **2**, is a full member of this family, as it regioselectively cleaves BT even at 40 °C (see below).

Catalytic Hydrogenolysis of Benzo[*b*]thiophene to 2-Ethylthiophenol. A. Autoclave Reactions. Irrespective of the catalyst precursor (either **1** or **3**), BT is selectively transformed into the 2-ethylthiophenolate anion; traces of the hydrogenation product DHBT are often formed (≤1%). The results obtained are reported in Table 1.

The production of DHBT decreases by increasing the base to catalyst ratio. The hydrogenolysis product may be recovered as the potassium salt K[*o*-S(C$_2$H$_4$)C$_2$H$_5$]; for product quantification, however, it is convenient to transform the thiolate salt into ETP by treatment with aqueous HCl. If the final reaction mixtures are not acidified, spontaneous oxidation of the thiophenolate product to bis(2-ethylphenyl) sulfide takes place upon

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(21) (a) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P.; Herrera, V.; Sánchez-Delgado, R. A. *J. Am. Chem. Soc.* **1993**, *115*, 2731. (b) Bianchini, C.; Jiménez, M. V.; Meli, A.; Moneti, S.; Vizza, F. *J. Organomet. Chem.* **1995**, *504*, 27. (c) Bianchini, C.; Casares, J. A.; Jiménez, M. V.; Meli, A.; Moneti, S.; Vizza, F.; Herrera, V.; Sánchez-Delgado, R. A. *Organometallics* **1995**, *14*, 4850. (d) Bianchini, C.; Frediani, P.; Herrera, V.; Jiménez, M. V.; Meli, A.; Rincón, L.; Sánchez-Delgado, R. A.; Vizza, F. *J. Am. Chem. Soc.* **1995**, *117*, 4333. (e) Bianchini, C.; Jiménez, M. V.; Meli, A.; Vizza, F. *Organometallics* **1995**, *14*, 3196. (f) Bianchini, C.; Meli, A.; Pohl, W.; Vizza, F.; Barbarella, G. *Organometallics* **1997**, *16*, 1517. (g) Bianchini, C.; Casares, J. A.; Masi, D.; Meli, A.; Pohl, W.; Vizza, F. *J. Organomet. Chem.* **1997**, *541*, 143.

Scheme 4

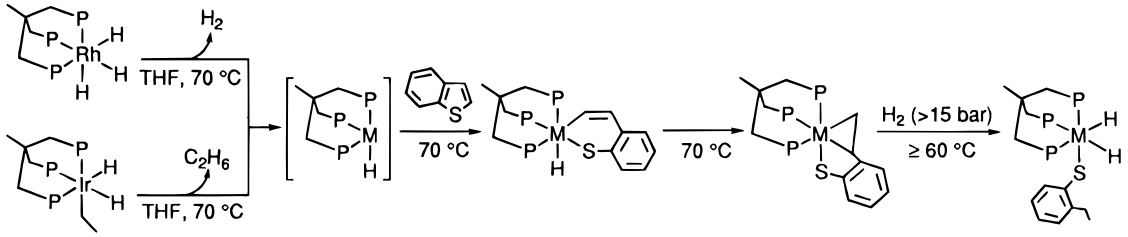
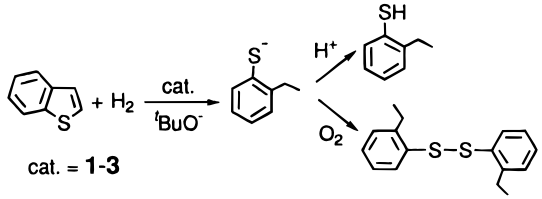


Table 1. Hydrogenolysis of Benzo[*b*]thiophene Catalyzed by [(triphos)Ru(H)BH_4] (1) and [(triphos)Ru(NCMe)$_3$](BPh_4)$_2$ (3) in the Presence of ^{t}BuOK[a]

entry no.	complex (amt, mmol)	amt of substrate, mmol	amt of base, mmol	*T*, °C	reacn mixture compositn, %[b] BT	ETP	DHBT	rate[c]
1	**1** (0.043)	4.3	4.3	160	32.5	67.1	0.4	0.58
2	**1** (0.043)	4.3	4.3	100	52.7	46.8	0.5	0.40
3[d]	**1** (0.043)	4.3	4.3	100	53.7	45.9	0.4	0.39
4	**1** (0.043)	4.3	0.3	100	95.3	3.6	1.1	0.03
5	**1** (0.043)	4.3	4.3	70	61.4	38.1	0.5	0.33
6[e]	**1** (0.043)	4.3	4.3	100	96.5	2.3	1.2	
7	**3** (0.043)	4.3	8.6	100	30.0	69.8	0.2	0.60
8	**3** (0.043)	4.3	4.3	100	55.6	43.9	0.5	0.38
9[f]	**3** (0.043)	4.3	4.3	100	56.8	42.8	0.4	0.37
10	**3** (0.043)	4.3	2.2	100	79.2	19.9	0.9	0.17
11	**3** (0.043)	4.3	1.1	100	82.6	16.8	0.6	0.14
12	**3** (0.043)	8.6	8.6	100	46.6	53.1	0.3	0.91
13	**3** (0.043)	8.6	4.3	100	75.6	23.9	0.5	0.41
14	**3** (0.086)	4.3	4.3	100	38.2	60.6	1.2	0.52
15	**3** (0.022)	4.3	4.3	100	68.2	31.4	0.4	0.27
16[e]	**3** (0.043)	4.3	4.3	100	99.1	0.2	0.7	
17	**3** (0.043)	4.3	4.3	70	68.2	31.2	0.6	0.27
18	**3** (0.043)	4.3	4.3	40	98.7	1.2	0.1	

[a] Reaction conditions: THF, 30 mL; H_2 pressure, 30 bar; time, 5 h. [b] Key: benzo[*b*]thiophene (BT), 2,3-dihydrobenzo]*b*]thiophene (DHBT), 2-ethylthiophenol (ETP). [c] Average rate expressed as (mmol of ETP) h^{-1}. [d] The reaction was carried out in the presence of elemental mercury. [e] THF/H_2O, 28:2 (v:v). [f] The reaction was carried out in the presence of PVP.

Scheme 5



exposure to air (Scheme 5).[22] For sake of clarity, the hydrogenolysis product, from now on, is referred to as ETP.

Effective catalytic transformation of BT occurs at 70 °C (entries 5 and 17), but even at 40 °C, ETP is formed in a concentration higher than the stoichiometric one (entry 18). At 100 °C and a 1:1 ratio between substrate and base, the hydrogenolysis rate, expressed as (mmol of ETP) h^{-1}, is ca. 0.4 (entries 2 and 8). This run has been considered as the standard reaction and has been studied in some detail in order to gain insight into the kinetics of the hydrogenolysis process.

The rate of conversion of BT dramatically depends on the base concentration, as shown by entries 2, 4, 7, 8, and 10−13. At a constant concentration of substrate and base, the rate increases with the catalyst concentration (compare entries 8 and 14, 15). The rate also increases with the temperature (entries 1, 2, 5 and 8, 17, 18). At the highest temperature investigated (160 °C), however, some decomposition of the catalyst occurs, as shown by the formation of some black precipitate in the reactor (entry 1). Atomic absorption analysis showed it to be metallic ruthenium. A sample of this solid precipitate was used as the catalyst precursor for the hydrogenation of BT, but no catalytic transformation was observed under comparable experimental conditions.

The presence of a substantial amount of water in the reaction mixture inhibits the hydrogenolysis of BT (entries 6 and 16) as a consequence of the formation of the dimer [(triphos)Ru(μ-$OH)_3$Ru(triphos)]$^+$ (**7**),[16] which independent reactions show to be catalytically inactive.

The addition of either elemental mercury or PVP to the catalytic mixtures did not significantly affect the overall conversion of BT (entries 3 and 9). These two experiments are thus consistent with a truly homogeneous process.[23,24]

The overall picture of the present hydrogenolysis of BT is quite similar to that of other reactions of this type catalyzed by the [(triphos)RhH] fragment in different phase-variation systems.[8] Linear correlations between the hydrogenolysis rate and the concentration of catalyst, substrate, or base are generally observed. The accelerating effect of the base has been attributed to the positive influence exerted by the base on the rate-determining step, *i.e.* the reductive elimination of the thiol from the metal center (*vide infra*).[8] In the case at hand, the influence of the base concentration on the hydrogenolysis rate is even more pronounced, as shown by the fact that the rate does not increase with the concentration of BT (entry 13) unless the concentration of KOBu^t is proportionally increased (entry 12). We ascribe this unusual effect to the great basicity of the trihydride **2** and hence of [(triphos)RuH]$^-$. Both these species rapidly react with water or alcohols to give the neutral dihydride fragment [(triphos)Ru($H)_2$] (see above), which current studies from this laboratory show to be unable to catalyze the hydrogenolysis of BT.[16] While the presence of water in the catalytic mixture can be extensively reduced and eventually suppressed by using freshly distilled THF over $LiAlH_4$, ^{t}BuOH cannot be avoided, as it is the conjugate acid of the base employed to generate the catalyst (any other base would have the same effect). A similar situation has been reported to occur for the two catalysts [*fac*-RuH_3($PPh_3)_3$]$^-$/[RuH_4-

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$(PPh_3)_3$], which have been found to coexist through the equilibrium (6) in the course of the hydrogenation of cyclohexanone to cyclohexanol.[19]

$$[RuH_3(PPh_3)_3]^- + c\text{-}C_6H_{11}OH \rightleftarrows [RuH_4(PPh_3)_3] + c\text{-}C_6H_{11}O^- \quad (6)$$

Only the addition of a very large excess of $KOBu^t$ as in entry 12 shifts to the left the analogous equilibrium involving **2** so as to cancel the presence of the tetrahydride complex **8** in the catalytic mixture (eq 7). For this

$$[(triphos)RuH_3]^- + {}^tBuOH \rightleftarrows [(triphos)RuH_4] + {}^tBuO^- \quad (7)$$

reason, besides accelerating the hydrogenolysis rate, a large excess of base in the catalytic mixtures also improves the chemoselectivity of the reactions. The production of DHBT decreases, in fact, by decreasing the concentration of the tetrahydro complex **8**, which is an effective catalyst for the hydrogenation of BT.[11]

B. HPNMR Studies. The hydrogenolysis of BT to ETP catalyzed by either **1** or **3** has been studied in an HPNMR tube under experimental conditions that are as close as possible to those employed in the standard batch reaction. The only significant differences are a higher concentration of the catalyst for a better resolution and acquisition of the NMR spectra and, obviously, a lower stirring rate. The head space of the 10 mm tubes is large enough to maintain a high concentration of H_2 into the solution (^1H NMR evidence). Indeed, we generally observe that the mass transfer of H_2 from the head space of the NMR tube is efficient enough to replenish the solution which is being depleted of this reagent by the catalyst.

A sequence of selected $^{31}P\{^1H\}$ NMR spectra is reported in Figure 2 for a reaction catalyzed by the hydride tetrahydroborate complex **1** (trace a; this trace represents the spectrum of a pure sample of **1** in THF-d_8 under nitrogen) in THF-d_8 with a BT:$KOBu^t$:**1** ratio of 30:10:1 under 30 bar of H_2. Even at room temperature, **1** transformed into **2** after ca. 1 h at 20 °C (trace b). In the course of this transformation, no reaction involving BT was observed by ^1H NMR spectroscopy. Increasing the temperature to 50 °C induced no change in the $^{31}P\{^1H\}$ NMR spectrum, whereas the ^1H NMR spectrum showed the appearance of resonances due to free 2-ethylthiophenolate (δ 3.04 (q, J(HH) = 7.4 Hz, CH_2CH_3), 1.31 (t, CH_2CH_3)). Only when the reaction mixture was heated to 70 °C did appreciable formation of the dihydride thiolate ruthenate **5** occur (trace c, after 30 min at 70 °C). No trace of the C−S insertion product **6** was detected spectroscopically, which is consistent with the fast hydrogenation of this complex to give **5**. With time **5** became the predominant ruthenium product (trace d, after 1 h at 70 °C). Spectra acquired over the following 3 h were practically identical with that of trace d, which indicated the attainment of a thermostationary state. ^1H NMR spectra acquired during the entire experiment at 70 °C (ca. 4 h) showed a gradual increase in the concentration of the 2-ethylthiophenolate product at the expense of that of BT. After the catalytic reaction was quenched by cooling to room temperature, **5** was the only metal product visible by $^{31}P\{^1H\}$ NMR spectroscopy (trace e). The tube was then removed from the spectrometer and depressurized to ambient pressure. The $^{31}P\{^1H\}$ NMR spectrum of this sample was identical with that of trace e. GC/MS analysis of the reaction mixture gave an 18% conversion of BT to ETP.

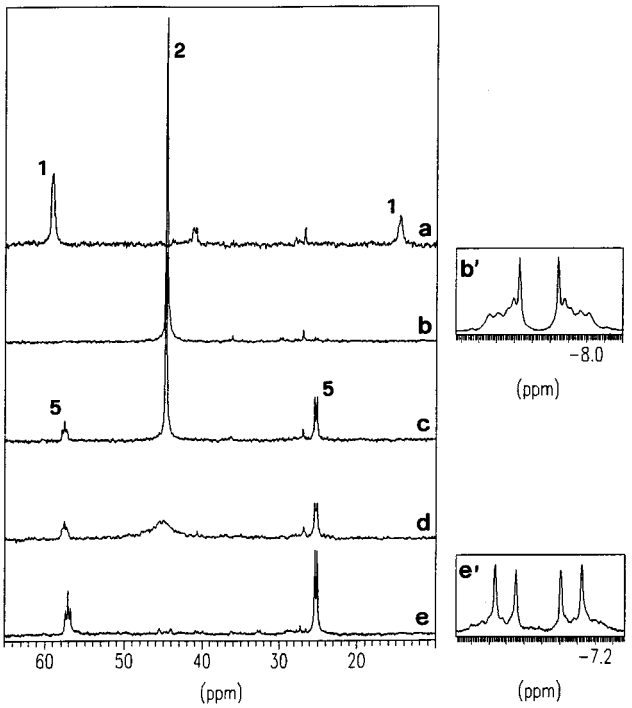

Figure 2. $^{31}P\{^1H\}$ NMR study (sapphire tube, THF-d_8, 81.01 MHz) of the catalytic hydrogenolysis of BT in the presence of **1** (30 bar of H_2, substrate:catalyst ratio 30, substrate:$KOBu^t$ ratio 10): (a) pure sample of **1**; (b) at 20 °C for 1 h; (c) at 70 °C for 30 min; (d) at 70 °C for 1 h; (e) after the tube was cooled to room temperature. In b′ and e′ are reported the ^1H HPNMR spectra (200.13 MHz) in the hydride region recorded immediately after the $^{31}P\{^1H\}$ NMR spectra b and e, respectively.

A sequence of selected $^{31}P\{^1H\}$ NMR spectra is reported in Figure 3 for the hydrogenolysis of BT catalyzed by the tris(acetonitrile) complex **3** under the same conditions of the reaction assisted by **1**. The transformation of the latter complex (trace a; this trace represents the spectrum of a pure sample of **3** in THF-d_8 under nitrogen) occurred even at room temperature, yielding **4** and three other unidentified minor species (trace b, after ca. 30 min at 20 °C). Increasing the temperature to 40 °C led to the gradual conversion of all the previously formed compounds to the ruthenate complex **5** (traces c−e, after 30 min, 90 min, and 3 h at 40 °C, respectively) *via* other species which are still unidentified. (Both **4** and all of these unidentified species were also seen in analogous experiments carried out at the same temperature and hydrogen pressure but in the absence of BT. Their rerlevance to catalysis is thus negligible. The final product of these blank experiments was the trihydride **2**.) During the course of the transformation of **3** into **5**, minor hydrogenation of BT to DHBT also occurred.[25] Only when the reaction mixture was heated to 70 °C was the formation of the trihydride **2** observed (trace f, after 30 min at 70 °C), and concomitantly, free ETP began to be produced. Spectra

(25) Complex **4**, which is an intermediate of **5**, is an excellent catalyst for the chemoselective hydrogenation of BT to DHBT.[11]

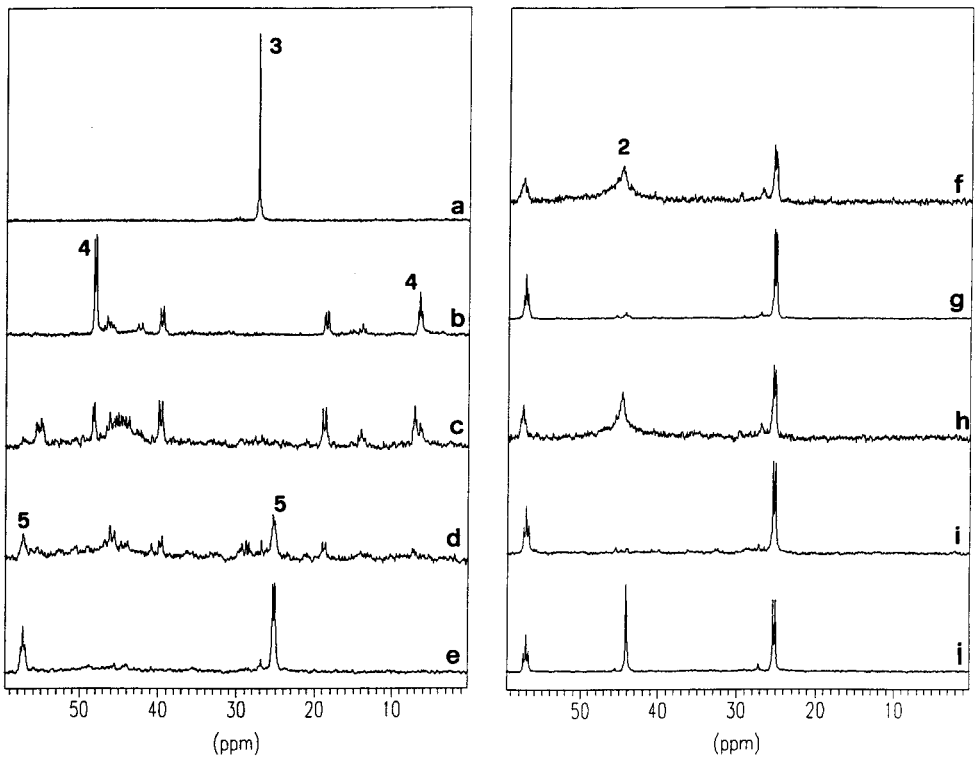

Figure 3. $^{31}P\{^1H\}$ NMR study (sapphire tube, THF-d_8, 81.01 MHz) of the catalytic hydrogenolysis of BT in the presence of **3** (30 bar of H_2, substrate/catalyst ratio 30, substrate/KOBu^t ratio 10): (a) pure sample of **3**; (b) at 20 °C for 30 min; (c) at 40 °C for 30 min; (d) at 40 °C for 1.5 h; (e) at 40 °C for 3 h; (f) at 70 °C for 30 min; (g) after the tube was cooled to 40 °C; (h) after the tube was heated to 70 °C for 30 min; (i) after 1 day at 20 °C.

acquired in the subsequent 1 h were practically identical with that of trace f. The NMR probe was cooled to 40 °C and heated again to 70 °C. $^{31}P\{^1H\}$ NMR spectra recorded at these two temperatures showed the disappearance (trace g, at 40 °C) and the re-formation of **2** (trace h, after 30 min at 70 °C). The ^1H NMR spectra acquired during the entire experiment at 70 °C (ca. 3 h) showed a gradual increase of the concentration of the 2-ethylthiophenolate product at the expense of that of BT, while the amount of DHBT formed in the first stage of the experiment did not increase during the entire experiment at 70 °C. After the catalytic reaction was quenched by cooling to room temperature, **5** was the only metal product visible by $^{31}P\{^1H\}$ NMR spectroscopy (trace i). GC/MS analysis of the contents of the tube gave the following product distribution: ETP (11%), BT (84%), DHBT (5%). The amines NH_2Et, $NHEt_2$, and NEt_3 in a ratio of 9:3:1 were also detected in the reaction mixture. In an identical experiment, after all **3** was transformed into **5** at the stage of trace i, the tube was removed from the spectrometer and set aside. The $^{31}P\{^1H\}$ NMR spectrum acquired after 1 day showed the formation (20%) of **2** at the expense of **5** (trace j).

In conclusion, the HPNMR studies suggest that **1** and **3** are precursors to the same catalytically active species. Indeed, the presence of the amine side products in the reactions assisted by **3** does not seem to have any mechanistic influence on the catalytic hydrogenolysis of BT. An interesting difference between the two catalyst precursors may be envisaged, however, in the mechanism of generation of the catalyst, *i.e.* the 16e$^-$ fragment [(triphos)RuH]$^-$. In the reactions assisted by **1**, the first metal complex to form is the trihydride ruthenate **2**, which cleaves the C_2-S bond of BT at 70 °C. As shown in Scheme 4 for the trihydride complex [(triphos)RhH_3], the reductive elimination of H_2 is a necessary step to generate the 16e$^-$ system [(triphos)-RhH], which ultimately inserts into the C_2-S bond of BT.[21] One may thus conclude that a temperature of 70 °C is required to promote the reductive elimination of H_2 from **2** and generate the fragment [(triphos)RuH]$^-$, which is electronically and sterically tailored for the cleavage of BT according to the reaction sequence summarized in Scheme 4.[21,26] HPNMR spectroscopy shows that the energy barrier to C−S insertion is much lower (40 °C) when **3** is employed as catalyst precursor. Moreover, the formation of the trihydride **2** does not precede the C−S bond cleavage, although **3** has been independently shown to react with H_2 and KOBu^t to give **2**. The different behavior of **3** may be interpreted assuming that the generation of the active Ru(0) fragment [(triphos)RuH]$^-$ proceeds *via* an alternative, lower energy reductive elimination reaction. For example, amine elimination from ruthenate complexes of the formula [(triphos)$Ru(H)_2(NR_2)$]$^-$ (R = H, Et; compounds of this type are common intermediates in transition-metal-catalyzed hydrogenation of nitriles[17] and imines[27]) may well account for the generation of [(triphos)RuH]$^-$. On the basis of this reasoning as well as previous reports,[20,21] one may readily conclude that also for ruthenium the energy barrier to C−S insertion by [(triphos)RuH]$^-$ is lower than that required to promote the elimination of H_2 from the corresponding trihydrido complex.

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Conclusions

In combination with a strong Brønsted base such as $KOBu^t$, the Ru(II) complexes [(triphos)RuH(BH_4)] (**1**) and [(triphos)Ru($NCMe)_3$]($BPh_4)_2$ (**3**) give rise to an efficient and selective homogeneous catalyst for the hydrogenolysis of BT to ETP in THF under mild reaction conditions (≥70 °C, 30 bar of H_2). Both precursors generate the same catalytically active species, *i.e.* the 16e$^-$ fragment [(triphos)RuH]$^-$. A clean precursor to this Ru(0) fragment is the ruthenate complex K[(triphos)RuH_3 (**2**), obtained by the reaction of $KOBu^t$ with **1**. In model studies at 70 °C, it has been shown that the trihydride **2** reacts with BT, yielding the 2-vinylthiophenolate complex K[(triphos)Ru(η^3-S(C_6H_4)CH=CH_2)] (**6**), which transforms into the 2-ethylthiophenolate product K[(triphos)Ru($H)_2$(*o*-S(C_6H_4)C_2H_5)] (**5**) by treatment with H_2. Under 30 bar of H_2, **5** is in equilibrium with the trihydride **2** and free ETP. At 70 °C, the equilibrium concentration of **2** increases with the concentration of $KOBu^t$ as a consequence of the accelerated elimination of ETP as K[*o*-S(C_6H_4)C_2H_5].

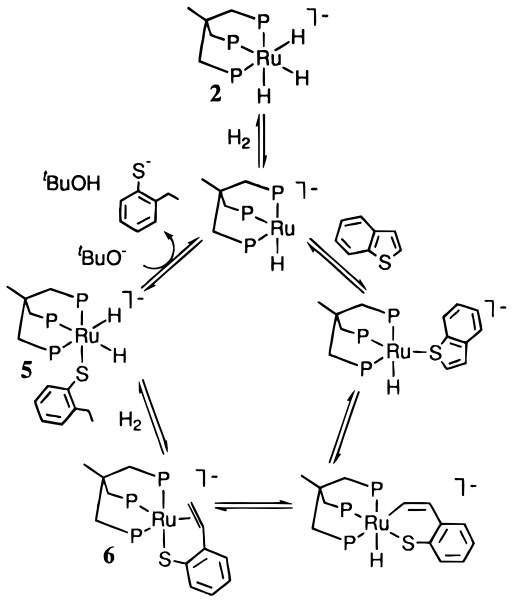
Irrespective of the catalyst precursor, ^{31}P HPNMR spectroscopy shows that the only detectable ruthenium complexes under catalytic conditions are **5** and **2** in equilibrium concentrations that depend on both the temperature and the amount of added base.

The intermediacy of DHBT in the hydrogenolysis of BT has been ruled out by several experiments. These include *in situ* NMR spectroscopy, which shows that **2** reacts with BT at 70 °C to yield the C−S insertion product **5**, whereas at this temperature DHBT is not transformed.

On the basis of all of this experimental evidence, one may conclude that the conversion of BT to ETP described in this paper takes place through the mechanism already established for the base-assisted hydrogenolysis of thiophenes catalyzed by [(triphos)MH] fragments (M = Rh, Ir).[8] The mechanism, illustrated in Scheme 6 for the [(triphos)RuH]$^-$ catalyst, involves the usual steps of C−S insertion, hydrogenation of the C−S-inserted thiophene to the corresponding thiolate, and base-assisted reductive elimination of the thiol to complete the cycle. Also in the case of ruthenium (HPNMR evidence, rate-accelerating effect of the base), the removal of the thiol product from the dihydride thiolate intermediate is proposed to be the rate-determining step.

In the course of the catalytic reactions, small quantities (≤1%) of the hydrogenation product DHBT are often produced, particularly in the reactions with base to substrate ratios lower than 1. The formation of DHBT can further be reduced by increasing the concentration of the base so as to minimize the presence of the tetrahydride complex [(triphos)RuH_4] (**8**) in the catalytic

Scheme 6



mixtures. Complex **8** is a selective catalyst for the hydrogenation of BT to DHBT in fact. Accordingly, the Brønsted base can play three distinct roles in the present hydrogenolysis reactions: it promotes the formation of the catalyst [(triphos)RuH]$^-$ by heterolytic splitting of H_2, speeds up the reaction rates, and improves the chemoselectivity.

As a final consideration, we wish to stress that a novel trihydride Ru(II) complex with great potential in homogeneous catalysis has been synthesized. The ruthenate **2** is a very electron-rich complex which can generate highly reactive unsaturated fragments with different chemical properties by either thermolysis (*i.e.* the Ru(0) monohydride [(triphos)RuH]$^-$ or reaction with proton donors (*i.e.* the Ru(II) dihydride [(triphos)Ru($H)_2$]). Either fragment has already been found capable of effectively catalyzing the hydrogenation of various substrates such as thiophenes, ketones, nitriles, imines, olefins, and nitrogen-containing heterocycles (quinolines, pyrroles) with distinct mechansims and selectivities.[11]

Acknowledgment. A contract (PR1/C) from the Ministero dell'Ambiente of Italy and an international cooperation agreement between the CNR (Italy) and CONICIT (Venezuela) are gratefully acknowledged for financial support.

Supporting Information Available: Text giving relevant physicochemical characteristics of the complexes [(triphos)Ru(μ-$OH)_3$Ru(triphos)]BPh_4, [(triphos)RuH_4], [(triphos)RuH(μ-$H)_2$-HRu(triphos)], and [(triphos)Ru($H)_2$(CO)] (1 page). Ordering information is given on any current masthead page.

OM9800804