C−S Bond Cleavage of Benzo[*b*]thiophene at Ruthenium

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Received January 27, 1998

The ruthenium(II) (tetrahydroborate)hydride complex [(triphos)RuH(BH_4)] (**1**) reacts with benzo[*b*]thiophene (BT) in THF at 40 °C yielding, after 3 h, a mixture of four different compounds: [(triphos)RuH{BH_3(*o*-S(C_6H_4)CH_2CH_3)}] (**2**), [(triphos)Ru{η^4-S(C_6H_4)CH(CH_3)}] (**3**), [(triphos)RuH(μ-S(C_6H_4)CH_2CH_3)$_2$HRu(triphos)] (**4**), and [(triphos)RuH(μ-BH_4)HRu-(triphos)]$^+$ (**5**$^+$) (triphos = MeC(CH_2PPh_2)$_3$). After two further hours of reaction, **3** disappears and is completely converted to **4**. Further heating at 40 °C does not change the product composition (**2**, **4**, and **5**$^+$ in a 4:1.3:3 ratio). A variety of independent reactions with isolated compounds have been performed with the aim of elucidating the mechanism of the C−S insertion/hydrogenation of BT to the 2-ethylthiophenolate ligand. The μ-thiolate complex **4** reacts in THF with dihydrogen (≥160 °C, 30 bar H_2) or with HBF_4·OEt_2 (20 °C) yielding ethylbenzene and 2-ethylthiophenol, respectively. No reaction occurs with $LiHBEt_3$. All of the reactions and new complexes reported have been studied by multinuclear NMR spectroscopy. An X-ray analysis has been carried out on a single crystal of **2**.

Introduction

Hydrodesulfurization (HDS) catalysis is the process of removing sulfur as H_2S from crude petroleum to provide more processable and environmentally sound fuels. The HDS reaction is accomplished by means of heterogeneous molybdenum (or tungsten) sulfide catalysts which incorporate small amounts of sulfided late transition metals acting as *promoters*.[1] Among the transition-metal promoters, ruthenium forms the most active sulfide for the HDS of thiophenes,[2] but Ru-promoted catalysts are scarcely employed in actual hydrotreating reactors due to their facile poisoning.[1] Currently, industrial HDS catalysts almost invariably contain cobalt or nickel as promoters (Co(Ni)−Mo(W)−S phases).

On the basis of several model reactor studies[2] and the fact the Ru−Mo−S interaction phase is similar to the largely employed Co−Mo−S phase,[1,3] ruthenium might have great potential as a HDS promoter once the factors that are responsible for the deactivation of the catalysts in refining conditions are understood and hopefully bypassed. To this end, model studies applying soluble ruthenium complexes might contribute to elucidate the mechanisms through which ruthenium interacts with the various types of thiophenic substrates as well as the other contaminants in fossil fuels (nitrogen and oxygen heterocycles, metal compounds). Despite many recent research efforts in this direction,[4] information on the reactivity of ruthenium complexes toward thiophenic substrates is still scarce and essentially limited to the reactions with thiophene (T). Both C−H[5] and C−S[6,7] bond cleavage reactions of T have been reported to take place at ruthenium. However, in no case has the rupture of T been observed to occur by direct C−S insertion of ruthenium. In the known examples, C−S bond cleavage has invariably been achieved by action of either nucleophiles on Ru(II) η^5-T complexes[6,7a,b] or electrophiles on Ru(0) η^4-T complexes.[7c,d] The reactions between ruthenium complexes and fused-ring thiophenes such as benzo[*b*]thiophene (BT) or dibenzo[*b,d*]thiophene (DBT) have received even less attention than those with T.[4] To the best of our knowledge, only one example of

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S0276-7333(98)00051-X CCC: $15.00
Publication on Web 05/15/1998

C−S insertion of BT has been reported so far.[8] The scarcity of experimental data and the potential of ruthenium in HDS catalysis prompted us to carry out a systematic study of the interactions between ruthenium complexes and thiophenic molecules.

After many efforts, we have been able to find a soluble ruthenium(II) complex which is capable of cleaving BT without the cooperation of either a multimetallic structure or externally added reagents. This complex is the (tetrahydroborate)hydride derivative [(triphos)RuH(BH_4)][9] (**1**), which straightforwardly transforms BT into the 2-ethylthiophenolate ligand. A detailed account of this reaction and of further studies aimed at mimicking the HDS of BT are also reported here.

Experimental Section

General Information. All reactions and manipulations, except as stated otherwise, were routinely performed under a nitrogen atmosphere by using standard Schlenk techniques. High-temperature reactions and 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. The ruthenium complex [(triphos)RuH(BH_4)] (**1**) was prepared as previously described.[9] All of the isolated metal complexes were collected on sintered-glass frits and washed with appropriate solvents before being dried in a stream of nitrogen. Tetrahydrofuran (THF) and THF-d_8 were purified by distillation under nitrogen from $LiAlH_4$. Benzo[*b*]thiophene (99%, Aldrich) was sublimed prior to use. 2-Ethylthiophenol (90%), HBF_4·OEt_2 (85% solution in OEt_2), and BH_3·THF (1.0 M solution in THF) were purchased from Aldrich and used without further purification. All of the other reagents and chemicals were reagent grade and used as received by commercial suppliers. ^1H (200.13 MHz), $^{13}C\{^1H\}$ (50.32 MHz), and $^{31}P\{^1H\}$ (81.01 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, ^{13}C) or 85% H_3PO_4 (^{31}P). Broad-band and selective $^1H\{^{31}P\}$ NMR experiments were carried out on the Bruker ACP 200 instrument equipped with a 5-mm inverse probe and a BFX-5 amplifier device. ^{13}C-DEPT and $^1H,^1H$ 2D-COSY NMR experiments were conducted on the Bruker ACP 200 spectrometer. $^1H\{^{11}B\}$ and $^1H\{^{31}P\}$ NMR experiments on **2** were conducted on a Bruker Avance DRX 500 spectrometer using the decoupling sequence GARP. The $^{11}B\{^1H\}$ NMR spectrum of **2** was acquired on the same instrument oprerating at 160.47 MHz and calibrated against external $NaBPh_4$ in acetone-d_6 with downfield values taken as positive. 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, Italy).[10] *Note: Since high gas pressures are involved, safety precautions must be taken at all stages of studies involving high-pressure NMR tubes.* 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.

Reactions of [(Triphos)RuH(BH_4)] (1) with Benzo[*b*]thiophene (BT). In Situ NMR Studies. A 5 mm NMR tube was charged first with a solid sample of [(triphos)RuH(BH_4)] (**1**) (30 mg, 0.04 mmol) and then with a solution containing a 5-fold excess of BT (27 mg, 0.2 mmol) in THF-d_8 (1 mL) under nitrogen. After 2 freeze/pump/thaw cycles at −196 °C, the tube was flame sealed and then placed into a NMR probe at room temperature. The reaction was followed by variable-temperature $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. No reaction between **1** (unresolved AM_2 pattern at 14.6 and 59.1 ppm)[9] and BT occurred at room temperature within 1 h, while appreciable formation of the μ-BH_4 dimer [(triphos)RuH(μ-BH_4)HRu(triphos)]$^+$ (**5**$^+$) (singlet at 40.9 ppm)[11] took place. At 40 °C, the amount of **5**$^+$ sligthly increased and the new complex [(triphos)RuH{BH_3(*o*-S(C_6H_4)CH_2CH_3)}] (**2**) was already observed in the first $^{31}P\{^1H\}$ and ^1H NMR spectra ($^{31}P\{^1H\}$ NMR AMQ spin system, δ 51.6 (dd, $J(P_AP_M) = 39.5$ Hz, $J(P_AP_Q) = 23.4$ Hz, P_A), 44.4 (dd, $J(P_MP_Q) = 23.4$ Hz, P_M), 8.9 (t, P_Q); ^1H NMR δ 3.13 (dq, J(HH) = 14.9, 7.5 Hz, C*H*H′CH_3), 2.71 (dq, J(HH) = 14.9, 7.5 Hz, CH*H*′CH_3), 2.7−2.1 (m, CH_2P), 1.58 (q, J(HP) = 2.6 Hz, CH_3), 1.20 (t, J(HH) = 7.5 Hz, CHH′CH_3), −7.45 (dt, $J(HP_{trans}) = 96.8$ Hz, $J(HP_{cis}) = 18.7$ Hz, Ru−H_t), −8.45 (br, Ru−*H*−B)). Compound **2** was identified by comparison of its $^{31}P\{^1H\}$ and ^1H NMR spectra to those of an authentic specimen (see below). Subsequent $^{31}P\{^1H\}$ NMR spectra acquired within 3 h at a constant temperature of 40 °C showed a seemingly simple scenario. Complex **1** gradually disappeared, formed in its place were **2** and **5**$^+$. ^1H NMR spectroscopy showed, however, that the reaction between **1** and BT is much more complicated than it was apparent from the $^{31}P\{^1H\}$ NMR spectra. Indeed, at least two other ruthenium complexes were formed during the reaction, which were not detected by $^{31}P\{^1H\}$ NMR spectroscopy due to their high fluxionality on the ^{31}P NMR time scale. At 40 °C, the resonances of these products, which have been assigned the formulas [(triphos)Ru{η^4-S(C_6H_4)CH(CH_3)}] (**3**) and [(triphos)RuH(μ-S(C_6H_4)CH_2CH_3)$_2$HRu(triphos)] (**4**), respectively (vide infra), are in fact completely merged into the baseline (see below). The formation of **3** and **4** in the course of the reaction between **1** and BT was unambiguously shown by ^1H NMR spectroscopy (Figure 1). A quintet at δ −1.15 (J(H,H/P) = 5.3 Hz), attributed to the CH(C*H*$_3$) methyl hydrogens of the sulfur ligand in **3**, already appeared in the first ^1H NMR spectra (traces a, b). The amount of **3** increased with time, reaching its maximum after 3 h (trace c). At this stage of the reaction, a quartet at δ −1.35 (J(HP) = 20.6 Hz) due to the terminal hydrides in the dimeric complex **4** (see below) began to be visible (trace c). With time, the concentration of **3** decreased and concomitantly that of **4** increased (traces d, e). After 5 h at 40 °C, only **2**, **4**, and **5**$^+$ were detected in the reaction mixture (trace f). No change in the concentration of **4** was observed for a further 1 h heating. At the end of the experiment, **2**, **4**, and **5**$^+$ were detected in the ratios of 4:1.3:3 (based on ^1H NMR integration of the methyl resonance of triphos).

Several experiments were carried out in different conditions. (A) In the presence of an excess of (NMe_4)BH_4, the reaction between **1** and BT was faster and gave a 3:1 mixture of **2** and **4** in ca. 1 h. The dimer **5**$^+$ was formed in trace amounts (1−2%).

(B) When the reaction was carried out under 5 bar of H_2, **3** was never seen by NMR prior to the formation of **4**. After 3 h, compounds **2**, **4**, and **5**$^+$ were formed in a ca. 5:1:3 ratio.

(C) Only compounds **2** and **5**$^+$ in a 2:1 ratio were obtained when the reaction was performed in the presence of both H_2 (5 bar) and BH_3·THF (5-fold excess).

(D) Neither **4** nor **3** was seen when a 5-fold excess of BH_3·THF was added to the initial reaction mixture. After 3 h of

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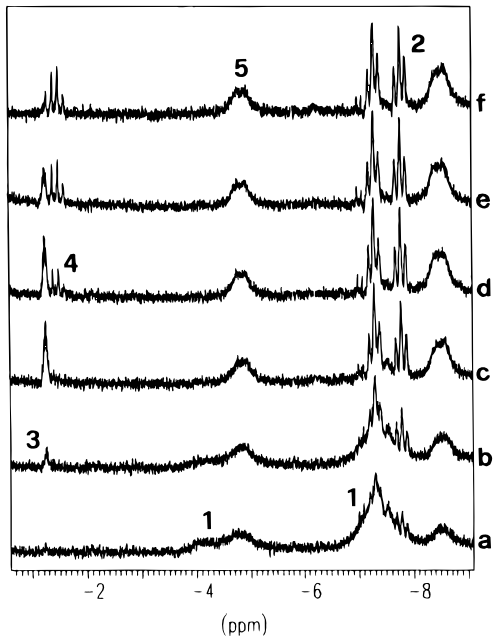


Figure 1. ^{1}H NMR study (THF-d_8, 200.13 MHz) of the reaction between **1** and BT at 40 °C: (a) after 0.5 h; (b) after 1 h; (c) after 3 h; (d) after 3.5 h; (e) after 4 h; (f) after 5 h.

heating at 40 °C, complexes **2** and **5**$^+$ were formed in a ca. 2:1 ratio.

(E) The selective formation of **2** occurred when the reaction between **1** and BT was carried out in the presence of a 5-fold excess of both $(NMe_4)BH_4$ and BH_3·THF.

NMR Characterization of [(Triphos)Ru{η^4-S(C_6H_4)CH(CH_3)}] (3). In an independent NMR experiment, carried out as described above, the tube was removed from the spectrometer when the amount of **3** reached its maximum (ca. 3 h). The tube was cooled to 0 °C and then reintroduced into the NMR probe at 0 °C. ^{1}H, ^{31}P{^{1}H}, and ^{1}H{^{31}P} NMR spectra were acquired in the temperature range from 0 to −60 °C. In this temperature range, **3** gave rise to a well-resolved ^{31}P AMQ spin system at −40 °C. ^{31}P{^{1}H} NMR (THF-d_8, −40 °C): AMQ spin system, δ 42.8 (dd, $J(P_AP_M)$ = 42.5 Hz, $J(P_AP_Q)$ = 18.6 Hz, P_A), 33.8 (dd, $J(P_MP_Q)$ = 26.1 Hz, P_M), 13.1 (dd, P_Q). ^{1}H NMR (THF-d_8, 0 °C): δ 2.95 (q, 1H, J(HH) = 5.7 Hz, C*H*CH$_3$), 2.6−2.2 (m, 6H, C*H*$_2$P), 1.59 (q, 3H, J(HP) = 2.6 Hz, C*H*$_3$), −1.18 (quint, 3H, J(HH) = 5.7 Hz, J(HP) = 5.1 Hz, CHC*H*$_3$). ^{1}H{^{31}P} NMR (THF-d_8, 0 °C): δ 2.95 (q, 1H, J(HH) = 5.7 Hz, C*H*CH$_3$), −1.18 (d, 3H, J(HH) = 5.7 Hz, CHC*H*$_3$).

Synthesis of [(Triphos)Ru(H){BH_3(*o*-S(C_6H_4)CH_2CH_3)}] (2). A. A mixture of **1** (300 mg, 0.4 mmol) and a 5-fold excess of BT (270 mg, 2 mmol) in THF (50 mL) was heated at 40 °C for 3 h with stirring. The resulting orange solution was concentrated to dryness. A portion of the residue, dissolved in THF-d_8 and analyzed by ^{31}P{^{1}H} and ^{1}H NMR spectroscopy, was found to contain **2**, **4**, and **5**$^+$ in ratios quite comparable to those observed in the corresponding NMR experiment. The rest of the residue was recrystallized from THF/ethanol to give **2** as well-shaped off-white crystals in 55% yield. Anal. Calcd (found) for $C_{49}H_{52}BP_3RuS$: C, 67.04 (66.81); H, 5.97 (5.89); Ru, 11.51 (11.31). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): AMQ spin system, δ 50.6 (dd, $J(P_AP_M)$ = 39.7 Hz, $J(P_AP_Q)$ = 23.1 Hz, P_A), 44.2 (dd, $J(P_MP_Q)$ = 23.1 Hz, P_M), 9.7 (t, P_Q). ^{1}H NMR (CD_2Cl_2, 20 °C): δ 2.96 (dq, 1H, J(HH) = 14.9 Hz, J(HH) = 7.5 Hz, CH*H*′CH$_3$), 2.61 (dq, 1H, J(HH) = 14.9 Hz, J(HH) = 7.5 Hz, CH*H*′CH$_3$), 2.55−1.95 (m, 6H, C*H*$_2$P), 1.47 (q, 3H, J(HP) = 2.7 Hz, C*H*$_3$), 1.10 (t, 3H, J(HH) = 7.5 Hz, CHH′C*H*$_3$), −7.55 (dt, 1H, $J(HP_{trans})$ = 96.5 Hz, $J(HP_{cis})$ = 18.9 Hz, Ru−*H*), −8.55 (br, 1H, $w_{1/2}$ = 72 Hz, Ru−*H*−B). ^{1}H{^{31}P} NMR (CD_2Cl_2, 20 °C): δ −7.55 (s, Ru−*H*), −8.55 (br, $w_{1/2}$ = 44 Hz, Ru−*H*−B). ^{1}H{^{11}B} NMR (CD_2Cl_2, 2 °C): δ 1.95 (br, B−*H*), −7.55 (dt, $J(HP_{trans})$ = 96.5 Hz, $J(HP_{cis})$ = 18.9 Hz, Ru−*H*), −8.55 (br d, J(HP) = 33.5 Hz, Ru−*H*−B). ^{11}B{^{1}H} NMR (CD_2Cl_2, 2 °C): δ −17.78 (br s, $w_{1/2}$ = 380 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 27.9 (s, *C*H$_2$CH$_3$), 15.4 (s, CH$_2$*C*H$_3$). IR: ν(B−H$_t$) 2423 (m), 2399 (s); ν(B−H$_b$) + ν(Ru−H$_t$) 1927 (br, m) cm^{-1}.

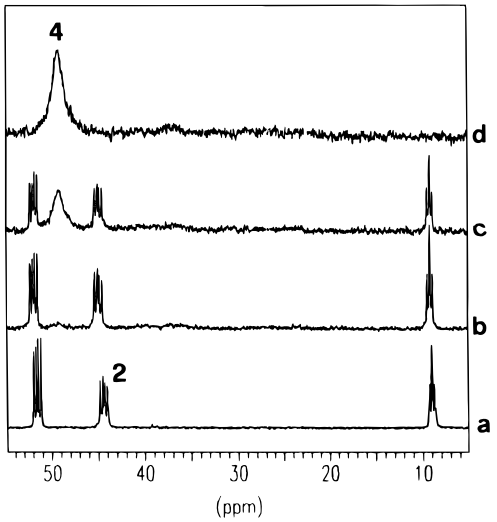


Figure 2. Variable-temperature ^{31}P{^{1}H} NMR study (THF-d_8, 81.01 MHz) of the thermal conversion of **2** to **4**: (a) at room temperature; (b) at 80 °C; (c) at 80 °C for 1 h; (d) at 80 °C for 4 h.

B. A THF (10 mL) solution of 2-ethylthiophenol (ETP) (60 μL, 0.4 mmol) was slowly added to a stirred solution of **1** (300 mg, 0.4 mmol) in THF (20 mL) at room temperature under nitrogen. After 30 min, the addition of ethanol (30 mL), followed by partial evaporation of the solvents under a steady stream of nitrogen, led to the precipitation of **2** in 85% yield.

Thermal Conversion of 2 to [(Triphos)RuH(μ-S(C_6H_4)CH_2CH_3)$_2$HRu(triphos)] (4). A. NMR Experiment. A 5 mm NMR tube was charged with a THF-d_8 solution (1 mL) of **2** (30 mg, 0.034 mmol) under nitrogen. After 2 freeze/pump/thaw cycles at −196 °C, the tube was flame sealed and then placed into a NMR probe at room temperature. The reaction was followed 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 2.

Compound **2** (trace a) was found to convert to **4** only when the probe head was heated to 80 °C (trace b); quantitative conversion occurred in ca. 4 h (trace d). Afterward, the temperature of the probe head was decreased to 60, 40, 20, 0, −20, −40, and −60 °C and ^{31}P{^{1}H} and ^{1}H NMR spectra were acquired at each temperature (Figure 3).

At 80 °C, the spectrum showed a unique broad signal centered at ca. δ 48.9, which is consistent with the fast exchange of the three phosphorus atoms of each triphos in the dimeric molecule (trace a). Decreasing the temperature to 60 °C resulted in the extensive broadening of the signal (trace b), which merged into the baseline below 40 °C (traces c, d). Decoalescence occurred above 0 °C. At −20 °C, an AM_2 pattern was clearly visible (trace e), which was completely resolved at −60 °C (trace f): δ 68.6 (d, $J(P_AP_M)$ = 18.3 Hz, P_A), 13.9 (t, P_M). In the ^{1}H NMR spectra, the resonance of the terminal hydride ligands appeared as a quartet in the temperature range from 80 to 20 °C and a well-resolved doublet of triplets at −60 °C. ^{1}H NMR (20 °C): δ 3.20 (q, 4H, J(HH) = 7.5 Hz, C*H*$_2$CH$_3$), 2.48 (d, 12H, J(HH) = 8.1 Hz, C*H*$_2$P), 1.75 (q, 6H, J(HP) = 2.7 Hz, C*H*$_3$), 1.45 (t, 6H, J(HH) = 7.5 Hz, CH$_2$C*H*$_3$), −1.31 (q, 2H, J(HP) = 20.8 Hz, Ru−*H*). ^{1}H NMR (−60 °C): δ −1.11 (dt, 2H, $J(HP_{trans})$ = 97.7 Hz, $J(HP_{cis})$ = 36.9 Hz, Ru−*H*).

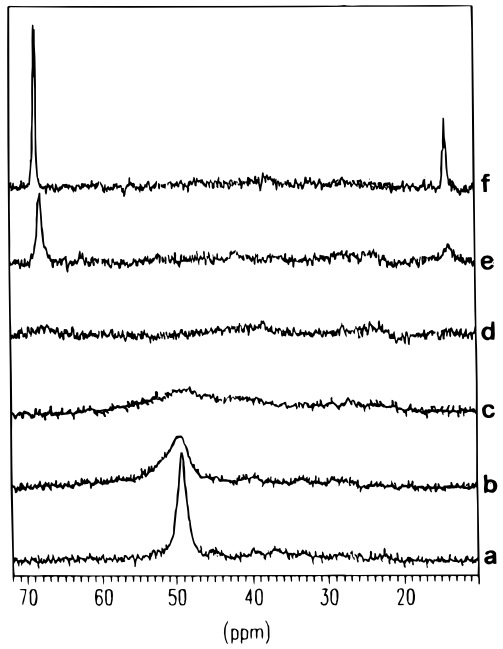


Figure 3. Variable-temperature $^{31}P\{^1H\}$ NMR spectra (THF-d_8, 81.01 MHz) of **4**: (a) 80 °C; (b) 60 °C; (c) 40 °C; (d) 0 °C; (e) −20 °C; (f) −60 °C.

B. Synthetic Experiment. A THF solution (50 mL) of **2** (300 mg, 0.34 mmol) was heated in a Parr reactor at 80 °C under nitrogen. After 5 h, the reactor was allowed to cool to room temperature. The reaction mixture was transferred into a Schlenk-type flask where it was concentrated to 5 mL in vacuo. Portionwise addition of *n*-heptane (ca. 40 mL) led to the precipitation of **4** as a yellow-orange solid, which was filtered off and washed with *n*-pentane; yield 90%. Anal. Calcd (found) for $C_{98}H_{98}P_6Ru_2S_2$: C, 68.12 (67.33); H, 5.72 (5.71); Ru, 11.70 (11.12). IR: ν(Ru−H) 1900 (m) cm^{-1}.

Reaction of 4 with BH_3·THF. NMR Experiment. A 5 mm NMR tube was charged first with a THF-d_8 solution (1 mL) of **4** (30 mg, 0.017 mmol) and then with a 10-fold excess of BH_3·THF under nitrogen. The $^{31}P\{^1H\}$ and ^1H NMR spectra of this sample showed the quantitative conversion of **4** to **2** at room temperature.

Reaction of 4 with HBF_4·THF or $LiHBEt_3$. NMR Experiment. A 5 mm NMR tube was charged first with a THF-d_8 solution (1 mL) of **4** (30 mg, 0.017 mmol) and then with a 2-fold excess of HBF_4·THF under nitrogen. The $^{31}P\{^1H\}$ and ^1H NMR spectra of this sample showed the quantitative formation of free ETP (^1H NMR δ 4.14 (s, S*H*), 2.78 (q, J(HH) = 7.4 Hz, CH_2CH$_3$), 1.31 (t, CH$_2$CH_3)) together with some unidentified ruthenium species.

Substitution of $LiHBEt_3$ for HBF_4·THF resulted in no transformation of **4** up to 80 °C.

Reaction of 4 with H_2. The thermolysis of **4** in the presence of H_2 (30 bar) was carried out in THF solution in a Parr reactor. No reaction occurred below 120 °C. At 160 °C, the starting complex decomposed to give ethylbenzene and traces of ETP (GC/MS analysis). No H_2S was evolved. The solvent was removed under reduced pressure, and the solid residue was analyzed by NMR spectroscopy, which showed the formation of several unidentified products.

X-ray Data Collection and Structure Determination of 2. Data were collected on a Enraf-Nonius CAD4 diffractometer. Unit cell dimensions were determined from the least-squares refinement of the angular settings of 25 carefully centered reflections. Three standard reflections, checked every 2 h, showed no decay. Intensity data were corrected for Lorentz−polarization effects. Atomic scattering factors were those reported by Cromer and Waber[12] with an anomalous dispersion correction taken from ref 13. Absorption correction was applied via ψ scan. All calculations were done on a DIGITAL DEC 2000 AXP workstation using the SHELX-97 program.[14] Crystallographic details are reported in Table 1. The structure was solved by direct methods using the SIR93 program.[15] An empirical absorpion correction was applied via ψ scans with transmission factors in the range 0.94−1.00. Refinement was done by full-matrix least-squares calculations, initially with isotropic thermal parameters and finally with anisotropic thermal parameters for the Ru and P atoms. The phenyl rings were treated as rigid bodies with D_{6h} symmetry, and hydrogen atoms were introduced at calculated positions. The final difference map was featureless.

Table 1. Summary of Crystallographic Data for 2

formula	$C_{49}H_{52}BP_3RuS$
mw	877.83
cryst size, mm	0.075 × 0.1 × 0.55
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	10.206(5)
b, Å	13.760(5)
c, Å	16.526(5)
α, deg	91.530(5)
β, deg	103.010(5)
γ, deg	104.980(5)
V, Å^3	2175.5(15)
Z	2
ρ_{calcd}, g cm^{-3}	1.340
abs coeff, mm^{-1}	0.540
F(000)	914
radiation, Å	Mo, 0.710 69
θ range, deg	2.54−21.97
index ranges	$-10 \le h \le 10$, $-14 \le k \le 14$, $0 \le l \le 17$
no. of reflns collected	5532
no. of indep reflns	5306 (R_{int} = 0.0264)
refinement method	full-matrix least squares on F^2
data/restraints/param	5306/0/177
goodness of fit on F^2	1.019
final R indices [$I > 2\sigma(I)$]	R1 = 0.0582, wR2 = 0.1351
R indices (all data)	R1 = 0.0965, wR2 = 0.1513
largest diff peak, e Å^{-3}	0.862
largest diff hole, e Å^{-3}	−0.507

Results and Discussion

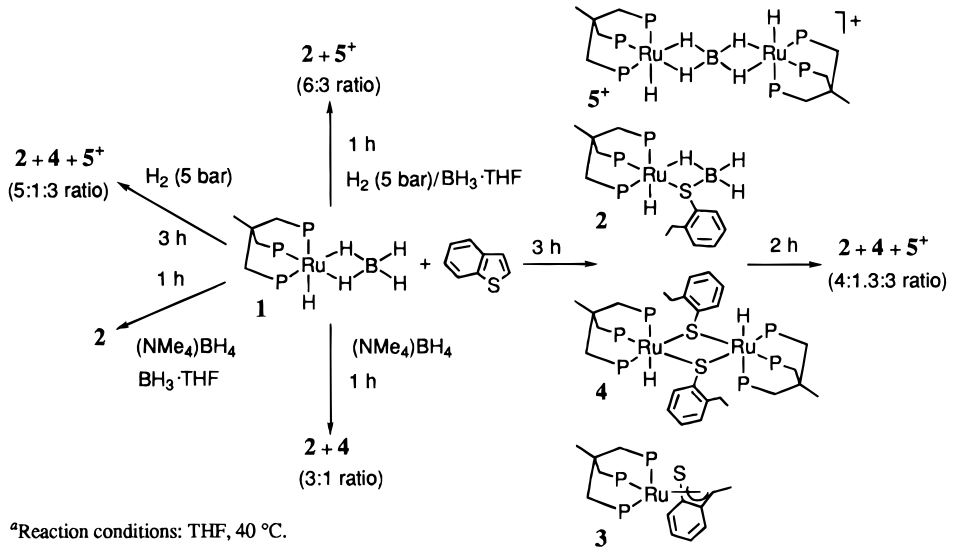
Characterization of the New Complexes. Four ruthenium complexes are produced upon the reaction of **1** with BT in THF at 40 °C (Scheme 1). Of these products, only [(triphos)Ru{η^4-S(C$_6$H$_4$)CH(CH$_3$)}] (**3**) has a fleeting existence and, for this reason, has been studied exclusively in solution. All of the other compounds have been isolated and adequately characterized in both the solid state and solution.

An X-ray analysis was carried out on a single crystal of the mononuclear C−S insertion/hydrogenation product [(triphos)RuH{BH$_3$(*o*-S(C$_6$H$_4$)CH$_2$CH$_3$)}] (**2**). Figure 4 shows a ZORTEP view of the molecule, while crystallographic data and selected bond distances and angles are listed in Tables 1 and 2, respectively.

The P$_3$Ru grouping of the (*fac*-triphos)Ru fragment has an approximate C_{3v} symmetry with three P−Ru−P

(12) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.
(13) *International Tables of Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4.
(14) Sheldrick, G. M. *SHELX-97 Program for Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.
(15) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

Scheme 1[a]



[a]Reaction conditions: THF, 40 °C.

[a] Reaction conditions: THF, 40 °C.

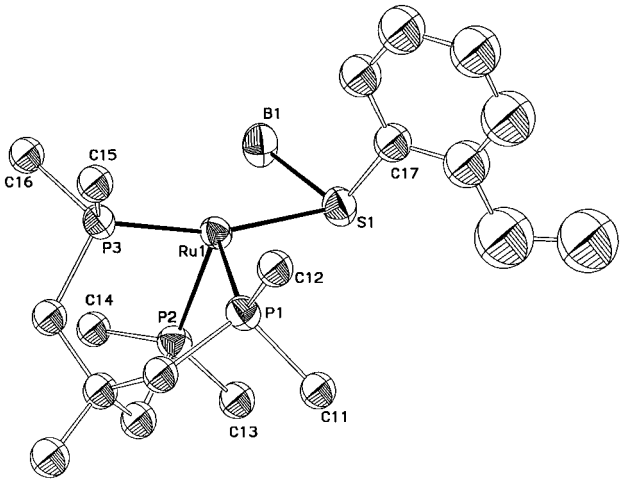


Figure 4. ZORTEP drawing of [(triphos)Ru(H){BH_3(*o*-$S(C_6H_4)CH_2CH_3$)}] (**2**). Phenyl rings of triphos are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 2

Distances	
Ru(1)−P(3)	2.251(2)
Ru(1)−P(1)	2.266(2)
Ru(1)−P(2)	2.359(2)
Ru(1)−S(1)	2.428(2)
S(1)−B(1)	1.911(9)
Angles	
P(3)−Ru(1)−P(1)	86.23(8)
P(3)−Ru(1)−P(2)	89.90(7)
P(1)−Ru(1)−P(2)	90.60(7)
P(3)−Ru(1)−S(1)	164.49(7)
P(1)−Ru(1)−S(1)	104.30(8)
P(2)−Ru(1)−S(1)	101.18(7)
C(17)−S(1)−B(1)	107.7(4)
C(17)−S(1)−Ru(1)	109.0(2)
B(1)-S(1)-Ru(1)	68.3(3)

angles in the range 86.23(8)−90.60(7)°. The Ru−S bond distance (2.428(2) Å) is comparable to those of ruthenium−thiolate complexes,[16] in particular, it is quite similar to the Ru−S distance in the C−S-inserted 2,5-dimethylthiophene complex [$CpRu(PPh_2Me)_2${η^1-SC(Me)=CHCH=(Me)}] (2.44(6) Å).[6b] No bonding interaction is envisaged between the Ru and B atoms (2.473(9) Å).[16] Neither the terminal hydride nor the bridging and terminal hydrogen atoms of the tetrahydroborate ligand could be located by X-ray diffraction. The presence and position of all of these hydrogen atoms have unambiguously been determined by NMR spectroscopy, however.

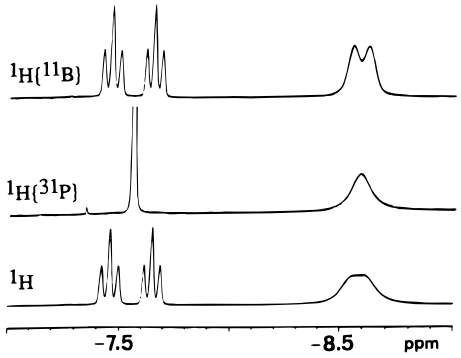


Figure 5. ^1H, $^1H\{^{31}P\}$, and $^1H\{^{11}B\}$ NMR spectra of **2** in the −7/−9 ppm region (500.13 MHz, CD_2Cl_2, 2 °C).

Complex **2** is stereochemically rigid on the NMR time scale up to 80 °C, at which temperature it starts decomposing to give the dimer [(triphos)RuH(μ-$S(C_6H_4)CH_2CH_3)_2$HRu(triphos)] (**4**) and BH_3. The $^{31}P\{^1H\}$ NMR spectrum consists of an AMQ pattern, typical of triphos metal complexes in which three different ligands are trans to the phosphorus donors. The terminal hydride H_t (δ −7.55) appears as a doublet of triplets in the ^1H NMR spectrum and becomes a singlet in the phosphorus-decoupled $^1H\{^{31}P\}$ spectrum (Figure 5). The position of H_t trans to P(2) is suggested by the long Ru−P(2) distance (2.359(2) Å) as well as the high-field ^{31}P NMR chemical shift of this phosphorus atom (9.7 ppm) (trans influence of the hydride).[17] The bridging Ru−H−B hydrogen atom (H_b) falls at slightly higher field (δ

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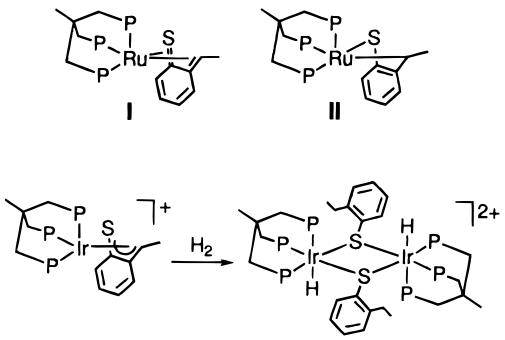
−8.55) than the terminal hydride and appears as a hump (trace a) which becomes a broad doublet with a J(HP) constant of 33.5 Hz in the $^1H\{^{11}B\}$ spectrum (Figure 5). The selective boron-decoupled ^1H NMR spectrum also allows the localization of the B−H hydrogens (δ 1.95) and unequivocally confirms our assignment. The $^{11}B\{^1H\}$ NMR spectrum shows a single, broad resonance at δ 17.78 which is typical of BH_4^- ligands.[18]

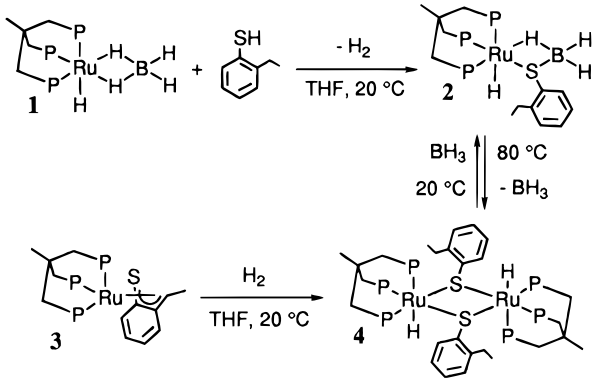
Unlike **2**, the identification of the dimers, **4** and $[(triphos)RuH(\mu\text{-}BH_4)HRu(triphos)]^+$ ($\mathbf{5}^+$) did not require a long investigation. The μ-BH_4 complex $\mathbf{5}^+$ was straightforwardly authenticated by comparing its spectroscopic characteristics with those reported in the literature by Venanzi et al.[11] A similar procedure was adopted to identify **4** as it belongs to a family of (μ-thiolate)hydride dimeric complexes of the formula $[(triphos)MH(\mu\text{-}SR)_2HM(triphos)]^{2+}$ (M = Rh, Ir; R = H,[19] Me,[19] C_8H_9,[20] $C_{12}H_9$,[21] $C_{20}H_{13}$[22]). In particular, **4** shares several chemical−physical properties with the closely related species $[(triphos)IrH(\mu\text{-}S(C_6H_4)CH_2CH_3)_2HIr(triphos)]^{2+}$ similarly obtained by C−S insertion/hydrogenation of BT.[20] Like the numerous Rh and Ir congeners, **4** is highly fluxional on the NMR time scale, the slow-exchange regime being attained at ca. −60 °C (^{31}P AM_2 pattern; ^1H doublet of triplets for the two equivalent terminal hydrides). The dynamic behavior of this class of dimeric compounds has been attributed to the flexibility of the thiolate bridges.[23]

In situ NMR (Figure 1) and model reaction studies (see below) clearly show that **3** is a precursor to **4** via hydrogen uptake. Indeed, from a comparison of the ^1H NMR spectra of **3** and **4**, one may readily realize that one of the H atoms added to the former complex generates a Ru−H bond while the other contributes to the formation of an ethyl group as neither hydride nor ethyl ligands are present in **3**. ^1H NMR spectroscopy, in combination with $^1H\{^{31}P\}$ and selective H,H-homonuclear decoupling NMR experiments, reveals the presence of a $CH(CH_3)$ group in **3** (quartet at δ 2.95 (CH) and quintet at δ −1.18 (CH_3, J(HH) = 5.7 Hz, J(HP) = 5.1 Hz)). The chemical shifts and the magnetic coupling pattern of this $CH(CH_3)$ grouping are typical of metal complexes containing the ligand $S(C_6H_4)CH(CH_3)$ which, depending on the metal oxidation state, may be formulated as either cyclohexadienthione (**I**) or thiophenolate (**II**) (Scheme 2).[20,24] In either case, the complex would be devoid of any symmetry which is consistent with the observed ^{31}P AMQ pattern for **3**. Moreover, all of the known complexes containing the $S(C_6H_4)CH(CH_3)$ ligand are analogously formed by metal-assisted transformation of BT and convert to the corresponding (μ-*o*-ethylthiophenolate) hydride dimers by treatment with H_2 (Scheme 2).[20]

Scheme 2



Scheme 3



On the basis of the spectroscopic and chemical evidence summarized above, **3** may be assigned a structure in which a *fac*-(triphos)Ru fragment is coordinated by a $S(C_6H_4)CH(CH_3)$ ligand. The transient nature of **3** in the experimental conditions leading to its formation does not allow one to discriminate between structures **I** and **II**, however. For this reason, we prefer to represent the thioligand in **3** with a delocalized electronic structure in all of the schemes reported in this paper.

Model Reactions. Several independent reactions have been carried out with the aim of confirming the structural assignments made above as well as getting insight into the mechanism of formation of the various products. The results of this study are illustrated in Schemes 1 and 3 and may be summarized as follows. (i) The presence of an excess of BH_4^- anions inhibits the formation of $\mathbf{5}^+$ but does not avoid the formation of **4**, which is conversely suppressed when BH_3·THF is added to the starting mixture. (ii) The conversion of **1** to $\mathbf{5}^+$ is a thermolytic process that occurs even in pure THF. Once formed, however, the μ-BH_4 dimer does not regenerate monomer **1**, even by treatment with a large excess of BH_4^- anions,[11] and is also inactive toward BT in the range of temperatures investigated. (iii) The selective formation of **2** takes place when both BH_4^- anions and BH_3·THF are added to the reaction mixture. Moreover, the presence of either reagent accelerates the C−S bond cleavage/hydrogenation reactions of BT. (iv) In the presence of H_2 (5 bar), the reaction between **1** and BT is complete in 3 h, yielding **2**, **4**, and $\mathbf{5}^+$.

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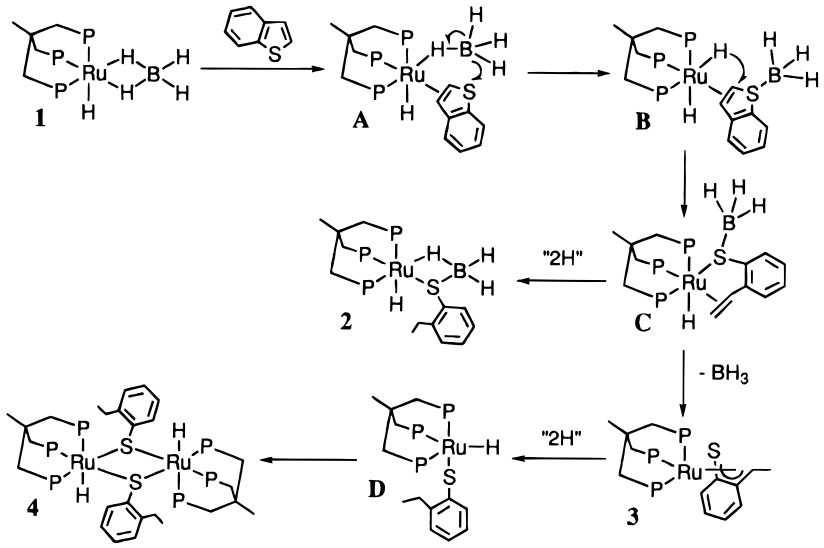
Scheme 4

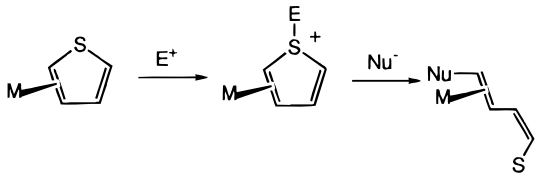


Complex **3** is not intercepted by NMR spectroscopy. (v) Complex **3** readily reacts with H_2 to give **4**. (vi) Complex **2** is thermally stable at 40 °C, thus it cannot generate **4** under the experimental conditions of the C−S insertion reaction. Only at 80 °C does the thermolysis of **2** slowly give **4**. (vii) Traces of free H_2 have been detected by ^{1}H NMR spectroscopy (singlet at 4.7 ppm) in the course of all reactions between **1** and BT.

Reaction between [(triphos)RuH(BH$_4$)] and Benzo[*b*]thiophene. As illustrated in Scheme 1, the reaction between **1** and BT is a quite complex process. However, with the contribution of in situ NMR spectroscopy, independent reactions using isolated compounds as well as relevant precedents in the literature, a rationalization of the chemical processes involved in the present C−S insertion/hydrogenation of BT may be proposed (Scheme 4).

In the mechanism reported in Scheme 4, a vacant coordination site at ruthenium for the incoming BT molecule is provided by the change of the bonding mode of the tetrahydroborate ligand in **1** from η^2 to η^1. Such hapticity changes have been invoked to account for both the fluxionality of tetrahydroborato metal complexes and their reactions with nucleophiles.[25] Moreover, the decoordination of the BH_4^- anion from **1**, which ultimately leads to the formation of $\mathbf{5}^+$, occurs readily at room temperature and reasonably proceeds via a stepwise unfastening of the two Ru−H−B bonds. Once a coordination vacancy has been created, BT may approach the metal center using either the sulfur atom or the C_2−C_3 double bond.[4,5] In the former case, direct C−S bond cleavage might take place if the metal center had sufficient electron density to be transferred into the C−S π*orbital.[4,26b] This path has never been observed for complexes with d^6 metal ions (e.g., Ru(II)), however, whereas it is quite common for d^8 metal complexes (e.g. Rh(I) and Ir(I)).[20,22,24a,b,26−28] If we, thus, assume that BT binds ruthenium through the C_2−C_3 double bond as shown in intermediate **A**, then the opening of BT would follow the general mechanism which involves the addition of electrophiles (in the case at hand BH_3) to the sulfur, followed by nucleophilic cleavage of the C−S bond by the hydride ligand.[27a,29] As an example, Scheme 5 summarizes the formation of 4-(alkylthio)-1,3-butadiene derivatives from Os(II) η^2-thiophene complexes reported by Harman and Spera.[29a]

Scheme 5



The formation of intermediate **C** (BT-derived analogues of this complex have precedents in the relevant literature)[21,24a,27a,e] may proceed by either a stepwise (**A** → **B**→ **C**) or concerted (**A** → **C**) process. Once formed, **C** evolves to **2** via hydrogenation of the vinyl group in the reducing environment of the reaction, which comprises BH_4^- anions generated by the partial conversion of **1** to $\mathbf{5}^+$ as well as H_2. In competition with the

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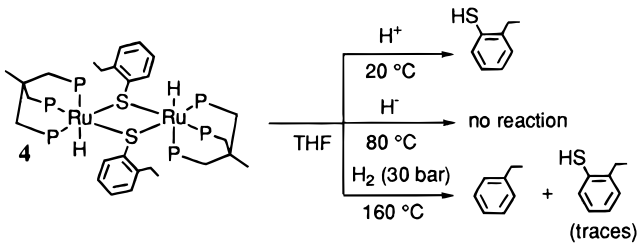
hydrogenation step and formation of **2**, **C** may convert to **3** via hydride migration to the external carbon atom of the double bond.[20,24] This step involves the loss of BH_3, consistent with the fact that the addition of an excess of BH_3 to the initial reaction mixture totally inhibits the formation of **3**. Moreover, the elimination of BH_3 from **2** to give **4** has been proved experimentally. Finally, hydrogenation of **3** yields the dimer **4** via the electronically and coordinatively unsaturated species **D**.

Given the evident complexity of the reaction between **1** and BT, our mechanistic interpretation, though accounting for all of the experimental observations, must be considered with extreme caution. Many of the proposed steps, if not all, however, are commonly encountered in the reactions of soluble metal complexes with thiophenes.

Reactions of [(Triphos)RuH(μ-S(C_6H_4)CH_2CH_3)$_2$-HRu(triphos)] with H^+, H^-, or H_2. Several examples of desulfurization of thiophenic substrates in fluid-phase systems have been reported to occur by reaction of metal complexes containing activated thiophenes with protic acids, hydride-releasing compounds, or H_2.[27a,30−34] The large majority of the homogeneous desulfurization reactions proceed through thiolate ligands (hydrogenolysis products), particularly when these bind simultaneously to two or more metal centers.[31−34] The rupture of the C−S bond of μ-alkylthiolate ligands with consequent formation of the desulfurized hydrocarbons and M=S moieties generally takes place at elevated temperatures and H_2 pressures. Similarly, we have found that the μ-*o*-ethylthiophenolate ligands are desulfurized to ethylbenzene only by heating **4** in THF to ≥160 °C under 30 bar of H_2 (Scheme 6).

Scheme 6



No reaction is observed when **4** is treated with $LiHBEt_3$, while ETP is liberated into the solution by reaction with $HBF_4{\cdot}OEt_2$ at room temperature.

Conclusions

The position of ruthenium in the activity trends for heterogeneous HDS is amply justified by the results obtained in this work. Indeed, the hydrogenolysis of BT assisted by **1** takes place in THF under reaction conditions (40 °C, traces of H_2), which are among the mildest ever observed. In the proposed mechanism, the C−S insertion step proceeds with the cooperation of both electrophilic and nucleophilic agents, which is consistent with several homogeneous and heterogeneous modeling studies. In line with the model studies, it has also been found that the multipoint coordination of the 2-ethylthiophenolate product is of crucial importance for the desulfurization step, which, however, requires a drastic increase in both temperature (≥160 °C) and pressure of H_2 (30 bar) to occur.

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

Supporting Information Available: Tables of final coordinates with equivalent isotropic thermal parameters (Table S1), bond distances and angles (Table S2), anisotropic thermal parameters (Table S3), and atomic coordinates of the hydrogen atoms (Table S4) for **2** (6 pages). Ordering information is given on any current masthead page.

OM980051T

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