

Mimicking the HDS Activity of Promoted Tungsten Catalysts. A Homogeneous Modeling Study Using a Two-Component Tungsten/Rhodium System

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Reaction of $W(CO)_5THF$ with $(triphos)Rh[\eta^3-S(C_6H_4)CH=CH_2]$ (**1**), obtained by insertion of the $16e^-$ fragment $[(triphos)RhH]$ into the C–S bond of benzo[*b*]thiophene (BT), gives the dimer $(triphos)Rh[\eta^3-(CO)_5WS(C_6H_4)CH=CH_2]$ (**2**; triphos = $MeC(CH_2PPh_2)_3$). Unlike **1**, the heterometal dimer **2** reacts with H_2 (30 atm) above 70 °C in THF, undergoing the desulfurization of the C–S-inserted BT. As a result, a mixture of the hydrido carbonyl species $(triphos)RhH(CO)$, ethylbenzene, and WS_x ($x_{av} = 1.5$) is obtained. High-pressure NMR spectroscopy in the temperature range from 20 to 70 °C shows that the desulfurization step is preceded by the formation by the dimer $(triphos)RhH(\mu-H)[\mu-o-S(C_6H_4)C_2H_5]W(CO)_4$ (**5**), in which the Rh and W centers are held together by bridging 2-ethylthiophenolate and hydride ligands. Complex **5** has been characterized in both the solid state (single-crystal X-ray analysis) and solution (multinuclear NMR spectroscopy). The desulfurization of **5** occurs also by thermolysis in THF at 120 °C under a nitrogen atmosphere. Reaction of **5** with CO (30 atm, 40 °C) gives the complex $[(triphos)Rh(CO)_2][(\mu-CO)_5W(o-S(C_6H_4)C_2H_5)]$ (**8**), in which the thiolate ligand is η^1-S bound to the tungsten atom in the complex anion $[(CO)_5W(o-S(C_6H_4)C_2H_5)]^-$. The hydrogenation of **8** (30 atm of H_2 , > 70 °C) gives exclusively free 2-ethylthiophenol. The carbonylation of **2** (30 atm of CO, room temperature) results in the formation of $[(triphos)Rh(CO)_2][(\mu-CO)_5W(o-S(C_6H_4)CH=CH_2)]$ (**3**), in which the 2-vinylthiophenolate ligand is η^1-S bound to the tungsten atom. The possible similarity in the C–S bond cleavage mechanism in the desulfurization of **5** to those occurring in the HDS over promoted heterogeneous catalysts is discussed.

Introduction

Due to environmental concerns, increasing research attention is being paid to the development of more efficient technologies for sulfur removal in crude oil. The existing processes can hardly reduce the sulfur contents in fuels to the internationally agreed level of 100 ppm and most likely will be unable to meet new standards dictated by stricter pollution regulations.¹ In refineries, sulfur, in the form of various organosulfur compounds among which the thiophenes are the most difficult to degrade, is eliminated from crude oil as H_2S (later disposed of via the Claus process)² by treatment with a high pressure of H_2 over hot heterogeneous catalysts.³ This process is referred to as hydrodesulfurization (HDS) and is typically catalyzed by metal sulfides deposited on a support; Mo and W are essential *components*, but increased catalytic activity, particularly toward the thiophenes, is observed when the catalyst

also comprises late transition metals.^{3,4} These are termed *promoters* and almost exclusively belong to group 8 (Co, Rh, Ir, Ru, Os, Ni, Pd, Pt).

Despite the huge amount of studies dealing with the structure and activity of heterogeneous HDS catalysts, particularly those classified as “Co/Mo/S” phase,^{3a} little is known about the chemical role played by the promoter metal atom. It is generally agreed that the promotion may be due to the creation of new sites with chemical–physical properties different from those responsible for the HDS by unpromoted catalysts or single-component catalysts containing only metal promoter sulfides.^{3a} For the specific case of the thiophenes, it has been suggested that the active centers for the activation of the substrate are the promoter atoms located at the edge plane of a WS_2 (MoS_2) single slab, whereas H_2 activation occurs on WS_2 (MoS_2) to give hydrosulphy species.^{4a} Consis-

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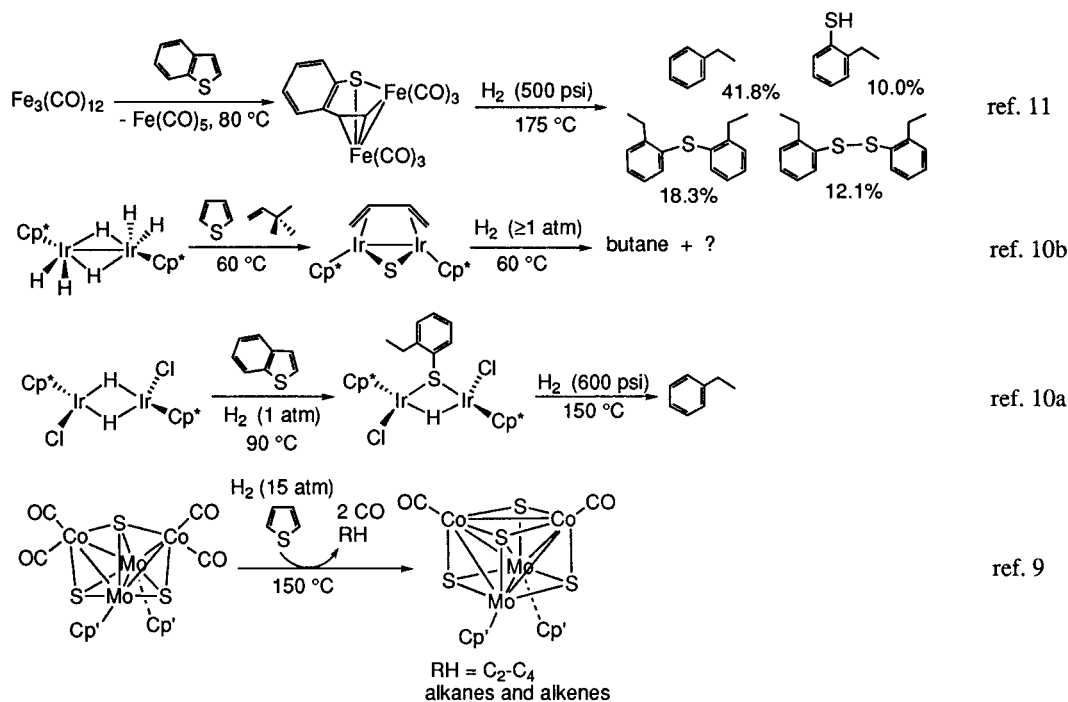
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Scheme 1



tently, both the binding of the thiophene directly to the promoter and the presence of Mo-SH groups on the surface of Co/Mo/S phase catalysts have been shown by EXAFS measurements.^{3a} Many other salient features of the HDS process regarding the specific and/or synergic role of the component and of the promoter in crucial steps of the HDS process are still rather obscure, however (e.g., C-S insertion, C-S cleavage, removal of surface sulfur, hydrogen transfer from M-SH groups to activated thiophene).

In order to gain insight into the mechanism of the many steps occurring in the heterogeneous HDS and ultimately assist in the design of improved catalysts, considerable effort is being directed toward the study of model systems involving soluble metal complexes and thiophenes. Indeed, many types of reactions between discrete organometallic complexes and thiophenes occur also on the surface of heterogeneous catalysts, and the mechanistic understanding obtained in solution has been applied to elucidate surface phenomena.⁵ With the advent of sophisticated physical-chemical techniques in solution, e.g., high-pressure NMR spectroscopy⁶ and transient UV flash kinetic spectroscopy,⁷ several breakthroughs have recently been obtained that, *inter alia*, have largely contributed to design alternative strategies,

such as aqueous biphasic catalysis, for sulfur removal in distillates.^{6a,8}

From a perusal of the homogeneous studies recently reviewed,⁵ one may readily infer that C-S bond scission in thiophenes is almost exclusively brought about by promoter metal complexes. In analogy to heterogeneous catalysts, however, the desulfurization step to H₂S and hydrocarbons has been observed to occur in solution only using either polymetallic species or external sources of "activated" hydrogen.^{5b,9-13}

Selected examples of HDS of thiophenes by soluble organometallic complexes are shown in Scheme 1. Among these, the Co/Mo/S cluster described by Curtis and co-workers is the model that more closely resembles the heterogeneous counterparts in terms of both structural motif and HDS activity (the hydrogen atoms necessary for the hydrogenolysis step are externally added and not already incorporated into the organometallic precursor). More recently, the Co/Mo/S cluster has successfully been employed to show that the C-S bond scission in the desulfurization of aromatic and aliphatic thiols may occur in a homolytic fashion and that thiolate and sulfido groups can move over the face of the cluster as they are supposed to do over the surface of Co/Mo/S phase catalysts.¹⁴ Both of these aspects, e.g., the cooperation of component and promoter metals in the

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desulfurization step and the walking of the thiolate from one metal to another, have attracted our attention within a long-lasting research project on HDS modeling. We have, for example, demonstrated that the 16e⁻ fragment [(triphos)RhH] cleaves almost any kind of thiophenic substrate to give C–S insertion products¹⁵ that behave as catalyst precursors for the hydrogenolysis of thiophene,^{6b} benzo[*b*]thiophene,^{6b,d} dibenzo[*b,d*]thiophene,^{6b} and dinaphtho[2,1-*b*:1',2'-*d'*]thiophene^{6c} to the corresponding thiols (triphos = MeC(CH₂PPh₂)₃). In no case was the desulfurization of the thiol product observed in a clear homogeneous process even under drastic reaction conditions, however. We therefore decided to examine the chemistry of a typical rhodium C–S insertion product appropriately modified so as to contain tungsten bound to the sulfur atom. To this end, we synthesized the benzo[*b*]thiophene-derived heterometal complex (triphos)Rh[η³-(CO)₅WS(C₆H₄)CH=CH₂] and were gratified to find that the hydrogenation of this dimer indeed results in the desulfurization of the cleaved thiophene though a well-defined intermediate species. Also, we discovered that the slippage of the thiolate fragment from the Rh promoter, responsible for the C–S insertion, to the W component can occur by addition of a nucleophile to the heterometal dimer.

The present paper constitutes a detailed account of this study, part of which was previously communicated.¹⁶

Experimental Section

General Information. All reactions, manipulations, and chromatographic separations (except as stated otherwise) were routinely performed under a nitrogen atmosphere by using standard Schlenk techniques. Tetrahydrofuran (THF) was distilled from LiAlH₄, stored over molecular sieves, and purged with nitrogen prior to use. Benzo[*b*]thiophene (BT, Aldrich) was sublimed prior to use. All other chemicals were commercial products and were used as received without further purification. (triphos)Rh[η³-S(C₆H₄)CH=CH₂]^{15b} and (triphos)-WH₆¹⁷ were prepared as previously described. All metal complexes were collected on sintered-glass frits and washed with appropriate solvents before being dried under a stream of nitrogen. Photochemical reactions were performed by using a Helios Italquartz UV 13F apparatus. The photolysis source was a 135 W (principal emission wavelength 366 nm) high-pressure mercury vapor immersion lamp equipped with a water filter to remove excess heat. Reactions under controlled pressure of hydrogen or carbon monoxide were performed with a Parr 4565 reactor equipped with a Parr 4842 temperature and pressure controller. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FT-IR spectrophotometer using either samples mullied in Nujol between KBr plates or THF and CH₂Cl₂ solutions. Deuterated solvents for NMR measurements were dried over molecular sieves. ¹H (200.13 MHz), ¹³C-{¹H} (50.32 MHz), and ³¹P-{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, ¹³C) or 85% H₃PO₄ (³¹P). Broad-band and selective ¹H-{³¹P} NMR experiments were carried out on the Bruker ACP

200 instrument equipped with a 5 mm inverse probe and a BFX-5 amplifier device. ¹³C-DEPT, ¹H,¹³C 2D-HETCOR, and ¹H,¹H 2D-COSY NMR experiments were conducted on the Bruker ACP 200 spectrometer. 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).¹⁸ *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 LAOCN3¹⁹ and Davins²⁰ running on a Compaq Deskpro 386/25 personal computer. The initial choices of shifts and coupling constants were refined by iterative least-squares calculations using experimental digitized spectra. The final parameters gave a satisfactory fit between 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 FT) 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.

Synthesis of (triphos)Rh[η³-(CO)₅WS(C₆H₄)CH=CH₂](2)**.** A sample of W(CO)₆ (0.12 g, 0.33 mmol), dissolved in THF (30 mL), was placed in a quartz reactor and converted to W(CO)₅(THF) by photolysis at -10 to +10 °C under a flow of nitrogen. After 4 h, this solution was cannulated into a flask containing (triphos)Rh[η³-S(C₆H₄)CH=CH₂]**(1)** (0.28 g, 0.33 mmol) in THF (20 mL) and the resulting mixture stirred for 1 h at room temperature. The volume of the solvent was reduced to ca. 15 mL and ethanol (40 mL) was added. Orange-yellow microcrystals of **2** were obtained in 85% yield after filtering, washing (ethanol and *n*-pentane), and drying. Anal. Calcd (found) for C₅₄H₄₆O₅P₃RhSW: C, 54.65 (54.55); H, 3.91 (3.81); Rh, 8.67 (8.49). IR: ν(CO) 2060 (m), 1966 (m), 1917 (vs), 1872 (s) cm⁻¹. ³¹P{¹H} NMR (CD₂Cl₂, 20 °C): AMQX spin system, δ 30.9 (ddd, *J*(P_{APM}) = 36.0 Hz, *J*(P_{APQ}) = 32.0 Hz, *J*(P_{ARh}) = 115.8 Hz, P_A), -7.1 (ddd, *J*(P_{MPQ}) = 42.6 Hz, *J*(P_{MRh}) = 112.4 Hz, P_M), -10.0 (ddd, *J*(P_{QRh}) = 104.6 Hz, P_Q). ¹H NMR (CD₂Cl₂, 20 °C): δ 3.84 (m, *J*(H₂H₃) = 9.5 Hz, *J*(H₂H₂) = 1.7 Hz, *J*(H₂Rh) = 1.8 Hz, H₂), 2.86 (m, *J*(H₃H₂) = 8.3 Hz, *J*(H₃-Rh) = 0.9 Hz, H₃), 2.70 (m, *J*(H₂Rh) = 1.5 Hz, H₂). The *J*(HH) and *J*(HRh) values were determined on the basis of ¹H{³¹P} NMR experiments. ¹³C{¹H} NMR (CD₂Cl₂, 20 °C): δ 42.5 (dm, *J*(CP) 35.9, C₂), 65.5 (dm, *J*(CP) 28.7, C₃), 200.1 (s, ¹⁸³W satellites with *J*(CW) = 128.7 Hz, CO_{eq}), 202.6 (s, CO_{ax}). The remaining ¹³C resonances were obscured by those of the triphos carbon atoms.

Reaction of 2 with Carbon Monoxide. A THF (50 mL) solution of **2** (0.24 g, 0.2 mmol) was reacted with CO (30 atm) at room temperature for 8 h in a Parr reactor. After the bomb was depressurized and vented under a nitrogen stream, the contents were transferred into a Schlenk-type flask. The volatiles were then removed in vacuo at room temperature, and a portion of the residue dissolved in CD₂Cl₂ was analyzed by NMR spectroscopy. In the ³¹P{¹H} NMR spectrum only the resonances due to the vinylthiophenolate complex **1** and the dicarbonyl [(triphos)Rh(CO)₂]⁺ (3:1 ratio) were observed.^{15b,21} Besides the resonances due to **1** and to the dicarbonylrhodium cation, the ¹H NMR spectrum showed a duo of doublets of doublets (δ 5.61, *J*(HH) = 17.6, 1.7 Hz; δ 5.26, *J*(HH) = 11.1, 1.7 Hz) characteristic of the *cis* and *trans* protons of a vinyl group. The rest of the residue was chromatographed on a silica column by using as eluants *n*-hexane to separate W(CO)₆, THF/*n*-hexane (1:1 ratio) to separate **1**, and THF to separate

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[(triphos)Rh(CO)₂][(CO)₅W(*o*-S(C₆H₄)CH=CH₂)] (**3**). This product was characterized on the basis of IR and ¹H and ³¹P{¹H} NMR spectroscopy. IR (THF): ν(CO) 2060 (s), 1990 (s), 1916 (s), 1852 (m) cm⁻¹. ¹H NMR (CD₂Cl₂, 20 °C): cation, δ 7.8–6.8 (m, Ph triphos), 2.61 (m, CH₂ triphos), 1.83 (q, *J*(HP) = 3.8 Hz, CH₃ triphos); anion, δ 7.1 (H₃, masked by the aromatic protons of triphos; the chemical shift was determined by a ¹H–¹H 2D-COSY experiment), 5.61 (dd, *J*(H_{2trans}H₃) = 17.6 Hz, *J*(H_{2trans}H_{2cis}) = 1.7 Hz, H_{2trans}), 5.26 (dd, *J*(H_{2cis}H₃) = 11.1, H_{2cis}), remaining resonances were obscured by those of the aromatic protons of triphos. ³¹P{¹H} NMR (CD₂Cl₂, 20 °C): δ 8.7 (d, *J*(PRh) = 98.6 Hz).

Reaction of 3 with [NBu₄]I. A THF (30 mL) solution of **3** (0.15 g, 0.12 mmol) was treated with an equimolar amount of [NBu₄]I (0.05 g, 0.14 mmol) at room temperature for 10 h. Chromatography on a silica column, with first THF/*n*-hexane (1:1 ratio) and then pure THF as eluants, gave (triphos)Rh(CO)₂²¹ and [NBu₄][(CO)₅W(*o*-S(C₆H₄)CH=CH₂)] (**4**; yield 80%), respectively. Anal. Calcd (found) for C₂₉H₄₃NO₅SW: C, 49.65 (49.06); H, 6.18 (6.19); N, 2.00 (1.89); S, 4.57 (4.32). IR (THF): ν(CO) 2055 (w), 1914 (s), 1851 (m) cm⁻¹. ¹H NMR (THF-*d*₆, 20 °C): cation, δ 3.51 (m), 1.88 (m), 1.57 (m), 1.15 (t); anion, δ 7.4–6.9 (m, C₆H₄), 7.13 (dd, *J*(H₃H_{2trans}) = 17.5 Hz, *J*(H₃H_{2cis}) = 11.0 Hz, H₃), 5.69 (dd, *J*(H_{2trans}H_{2cis}) = 1.8 Hz, H_{2trans}), 5.30 (dd, H_{2cis}). ¹³C{¹H} NMR (THF-*d*₆, 20 °C): cation, δ 60.7 (NCH₂), 26.1 (CH₂CH₂), 21.8 (CH₂CH₃), 15.3 (CH₃); anion, δ 152.3 (C–S), 138.2 (C–C₃), 136.4 (C₃), 134.1 (C–H), 128.3 (C–H), 127.6 (C–H), 122.8 (C–H), 112.8 (C₂); carbonyls, δ 203.5 (ax), 199.5 (¹⁸³W satellites with *J*(CW) = 126.8 Hz, eq).

Reaction of 4 with MeI. A 3-fold excess of neat MeI (26 μL, 0.42 mmol) was syringed into a stirred solution of **4** (0.10 g, 0.14 mmol) in THF (30 mL) at room temperature. After 1 h, the solution was pumped to dryness at room temperature and the residue was chromatographed on a silica column (*n*-hexane as eluant). The organic phase was concentrated to dryness in vacuo, and the residue was characterized by ¹H NMR and GC/MS spectroscopy as *o*-(methylthio)styrene by comparison to an authentic specimen.^{15b,22}

Reactions of 2 with Hydrogen in a Sapphire HPNMR Tube. In a typical experiment, a 10-mm sapphire HPNMR tube was charged with a THF-*d*₈ (2 mL) solution of **2** (0.03 g, 0.025 mmol) under nitrogen, pressurized with hydrogen to 30 atm at room temperature and then placed into the NMR probe preheated at 70 °C. The reaction was monitored by ³¹P{¹H} and ¹H NMR spectroscopy. A sequence of spectra recorded during this experiment is reported in Figure 1. In the ³¹P{¹H} NMR spectrum recorded after ca. 1 h, the AMQX spin system of **2** (50%) was accompanied by that of (triphos)RhH(*μ*-H)[*μ*-*o*-S(C₆H₄)C₂H₅]W(CO)₄ (**5**) (see below). After a further 2 h, **5** was the only species detected in solution (Figure 1b). The probe was then heated to 80 °C and the ³¹P{¹H} NMR spectra, recorded at this temperature every 30 min, showed the slow but gradual conversion of **5** to the known hydrido carbonyl species (triphos)RhH(CO)₂²¹ (**6**). Increasing the temperature to 100 °C (Figure 1c) and 120 °C (Figure 1d) increased the conversion rate of **5** to **6**. The highest temperature investigated represents the technical limit of the HPNMR tube. At 120 °C complete conversion of **5** to **6** was achieved in ca. 1 h. Small amounts (5–10%) of the known (triphos)Rh(CO)[*o*-S(C₆H₄)C₂H₅]^{6d} (**7**) were also detected in solution at the end of the reaction. The probe was cooled to room temperature (Figure 1e), and the NMR tube was removed from the spectrometer. An insoluble material was found to be deposited on the wall of the tube. A sample of the solution, withdrawn and analyzed by GC and GC/MS, was found to contain almost a quantitative amount of ethylbenzene (based on **2**, *n*-octane as internal standard) and traces of W(CO)₆.

The hydrogenation reaction of **2** to give **5** was found to occur, although slowly, even at room temperature (20% in 3 days).

Reaction of 2 with Hydrogen. Synthesis of (triphos)-RhH(*μ*-H)[*μ*-*o*-S(C₆H₄)C₂H₅]W(CO)₄ (5**).** A THF (50 mL) solution of **2** (0.24 g, 0.2 mmol) was reacted with H₂ (30 atm) at 70 °C for 3 h in a Parr reactor. After the bomb was depressurized and vented under a nitrogen stream, the contents were transferred into a Schlenk-type flask. The solution was concentrated to ca. 20 mL under vacuum. Portionwise addition of *n*-heptane (10 mL) led to the precipitation of **5** as brick red crystals which were washed with *n*-pentane; yield 75%. Anal. Calcd (found) for C₅₃H₅₀O₄P₃RhSW: C, 54.75 (54.68); H, 4.33 (4.25); Rh, 8.85 (8.69). IR: Nujol mull, ν(Rh–H) 1995 (s), ν(CO) 2057 (w), 1868 (s), 1852 (s), 1811 (s) cm⁻¹; CH₂Cl₂, ν(Rh–H) 1996 (s), ν(CO) 2058 (w), 1872 (vs), 1860 (sh), 1822 (s) cm⁻¹. ³¹P{¹H} NMR (CD₂Cl₂, 20 °C): AMQX spin system, δ 23.1 (ddd, *J*(P_AP_M) = 34.1 Hz, *J*(P_AP_O) = 26.9 Hz, *J*(P_ARh) = 109.7 Hz, P_A), 13.6 (ddd, *J*(P_MP_O) = 21.7 Hz, *J*(P_MRh) = 105.5 Hz, P_M), –9.2 (ddd, *J*(P_ORh) = 74.5 Hz, P_O). ³¹P NMR (CD₂Cl₂, 20 °C): δ 23.1 (d, *J*(P_ARh) = 110 Hz, P_A), 13.6 (t, *J*(P_MH_A) = *J*(P_MRh) = 100 Hz, P_M), –9.2 (dd, *J*(P_ORh) = 75 Hz, *J*(P_OH₅) = 180 Hz, P_O). Variable-temperature ³¹P{¹H} NMR spectra (THF-*d*₈, 20–70 °C, sapphire tube) are reported in Figure 3. ¹H NMR (CD₂Cl₂, 20 °C): δ 2.63 (dq, *J*(H₃H₃) = 14.0 Hz, *J*(H₃H₂) = 7.4 Hz, H₃), 2.18 (dq, *J*(H₃H₂) = 7.4 Hz, H₃), 1.10 (t, H₂), –9.88 (dm, *J*(H₄–Rh) = 19.02 Hz, *J*(H₄H₅) = 5.45 Hz, *J*(H₄P_M) = 100.6 Hz, ¹⁸³W satellites with *J*(H₄W) = 34.2 Hz, H₄), –10.07 (dm, *J*(H₅Rh) = 6.76 Hz, *J*(H₅P_O) = 181.5 Hz, H₅). The *J*(HH), *J*(HRh), and *J*(HW) values were determined on the basis of ¹H{³¹P} NMR experiments. ¹³C{¹H} NMR (CD₂Cl₂, 20 °C): δ 213.9 (s, CO), 210.6 (d, *J*(CP) = 5.3 Hz, CO), 205.5 (d, *J*(CP) = 3.8 Hz, CO), 205.2 (d, *J*(CP) = 6.0 Hz, CO), 29.1 (s, C₂), 14.9 (s, C₃). Well-shaped crystals of (triphos)RhH(*μ*-H)[*μ*-*o*-S(C₆H₄)C₂H₅]W(CO)₄·CH₂Cl₂ (**5**·CH₂Cl₂) were obtained by slow crystallization of **5** from CH₂Cl₂ and ethanol under nitrogen at room temperature. Anal. Calcd (found) for C₅₄H₅₂Cl₂O₄P₃RhSW: C, 51.99 (51.21); H, 4.20 (4.22); Rh, 8.25 (8.12).

Reaction of 5 with Hydrogen in a Sapphire HPNMR Tube. A 10 mm sapphire HPNMR tube was charged with a THF-*d*₈ (2 mL) solution of **5** (0.03 g, 0.026 mmol) under nitrogen, pressurized with hydrogen to 30 atm at room temperature and then placed into the NMR probe preheated to 120 °C. The reaction was monitored by ³¹P{¹H} and ¹H NMR spectroscopy. Compound **5** was found to convert to **6** (quantitative conversion in ca. 3 h) together with both ethylbenzene and a black insoluble material containing W and S (*vide infra*).

Thermal Reaction of 5 under Nitrogen in a Sapphire HPNMR Tube. A 10 mm sapphire HPNMR tube was charged with a THF-*d*₈ (2 mL) solution of **5** (0.03 g, 0.026 mmol) under nitrogen at room temperature and then placed into the NMR probe preheated at 120 °C. The reaction was monitored by ³¹P{¹H} and ¹H NMR spectroscopy. Although accompanied by extensive decomposition to some unidentified species, both **6** and **7** were formed in a ca. 3:1 ratio.

Reaction of 2 (or 5) with Hydrogen at 120 °C in an Autoclave. A solution of **2** (or **5**, 0.15 mmol) in THF (50 mL) was placed into a Parr reactor, pressurized with hydrogen to 30 atm at room temperature, and heated to 120 °C with stirring. After ca. 4 h, the reactor was cooled to room temperature and slowly depressurized. The contents of the bomb were transferred into a Schlenk-type flask. An insoluble black material, formed during the reaction, was filtered off (ca. 30 mg) and analyzed by elemental analysis (C, H, N), atomic absorption (Rh, W), gravimetric methods (P, S), and IR spectroscopy; sulfur to tungsten ratios ranging from 1.3 to 1.8 were found over five preparations (average value of 1.5). A sample of the filtrate, analyzed by GC and GC/MS, showed the presence of a quantitative amount of ethylbenzene (*n*-octane as internal standard) and traces of W(CO)₆. The remainder of the solution was concentrated to dryness in vacuo, and the residue, dissolved in CD₂Cl₂, was studied by ¹H and ³¹P{¹H} NMR spectroscopy, which showed the complete

transformation of **2** (or **5**) into the hydrido carbonyl species (triphos)RhH(CO) (**6**). The known compound (triphos)Rh(*o*-S(C₆H₄)C₂H₅)(CO) (**7**) was also detected in solution (<8%).

Reaction of 5 with Carbon Monoxide in an HPNMR Tube. A 10 mm sapphire HPNMR tube was charged with a THF-*d*₈ (1.5 mL) solution of **5** (0.03 g, 0.026 mmol) under nitrogen and then pressurized with CO to 30 atm at room temperature. The reactions were followed by variable-temperature ³¹P{¹H} and ¹H NMR spectroscopy. No reaction occurred at room temperature within 1 h. At 40 °C, quantitative conversion of **5** to [(triphos)Rh(CO)₂][(CO)₅W(*o*-S(C₆H₄)C₂H₅)] (**8**) and H₂ (¹H NMR singlet at 4.6 ppm) occurred in ca. 2 h. Once formed, **8** is stable in THF solution under a nitrogen atmosphere. ¹H NMR (THF-*d*₈, 20 °C): cation, δ 7.8–6.8 (m, Ph triphos), 2.62 (m, CH₂ triphos), 1.89 (q, *J*(HP) = 3.8 Hz, CH₃ triphos); anion, δ 2.74 (q, *J*(H₃H₂) = 7.4 Hz, H₃), 1.18 (t, H₂), remaining resonances were obscured by those of the aromatic protons of triphos. ³¹P{¹H} NMR (THF-*d*₈, 20 °C): δ 9.5 (d, *J*(PRh) = 98.1 Hz).

Reaction of [(triphos)Rh(CO)₂][(CO)₅W(*o*-S(C₆H₄)C₂H₅)] (8**) with Hydrogen in an HPNMR Tube.** An HPNMR tube containing a sample of **8**, prepared as described above, was pressurized with H₂ to 30 atm at room temperature and was then placed into the NMR probe. The reaction was monitored by variable-temperature ¹H NMR spectroscopy. Even at 70 °C, free 2-ethylthiophenol (ETP) started appearing in the solution. After 1 h at 70 °C, the quantitative formation of ETP was shown by both ¹H NMR and GC/MS analysis of the contents of the tube after this was depressurized. W(CO)₆ was the only tungsten carbonyl complex detected, while no production of EB was observed.

Attempted Hydrodesulfurization Reactions of BT in the Presence of Catalytic Amounts of Single-Component Complexes. In a typical reaction, a solution of (triphos)WH₆ (**9**),¹⁷ (triphos)Mo(*η*⁶-C₆H₆) (**10**),²³ [(triphos)MoH(*η*⁶-C₆H₆)]BF₄ (**11**),²³ [Cp*WS₃](PPh₄) (**12**),²⁴ W(CO)₆, or W(CO)₅THF (0.025 mmol) and a 100-fold excess of BT (330 mg, 2.5 mmol) in THF (30 mL) were placed into a Parr reactor, pressurized with hydrogen to 30 atm at room temperature, heated to the desired temperature (50–200 °C), and then immediately stirred. After 3 h, the reactor was cooled to room temperature and slowly depressurized by bubbling the gaseous phase into an aqueous solution of Pb(II) acetate. No formation of PbS was observed. The contents of the reactor were transferred into a Schlenk-type flask. A sample of the solution was withdrawn and analyzed by GC and GC/MS. With all catalyst precursors investigated, no catalytic transformation of BT was observed. The tungsten hexahydrido complex transformed less than the stoichiometric amount of BT into a mixture of EB and DHBT, while no production of EB, DHBT, or ETP was found using **10–12**. No catalytic activity was observed for reactions performed in the presence of a large excess of either strong Brønsted bases (KOBU) or acids (HBF₄). In acidic media, the hydrogenation of the tungsten trisulfide **12** led to the evolution of some H₂S.

X-ray Data Collection and Structure Determination of 5·CH₂Cl₂. Intensities of a brick red crystal of 5·CH₂Cl₂ were collected on a Philips PW1100 FEBO diffractometer. A set of 25 carefully centered reflections having 10 < θ < 16.5° was used to determine the cell constants. Three standard reflections were measured every 2 h for the orientation and the intensity control. During data collection no decay for the specimen was noticed. Intensity data were corrected for Lorentz–polarization effects. Atomic scattering factors were those reported by Cromer and Waber,²⁵ with anomalous dispersion correction taken from ref 26. An empirical absorp-

Table 1. Summary of Crystallographic Data for 5·CH₂Cl₂

Crystal Parameters	
formula	C ₅₄ H ₅₂ Cl ₂ O ₄ P ₃ RhSW
mol wt	1247.65
cryst size, mm	0.4 × 0.05 × 0.12
cryst syst	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i> (No. 14)
<i>a</i> , Å	15.626(5)
<i>b</i> , Å	19.129(5)
<i>c</i> , Å	17.270(5)
β, deg	92.33(1)
<i>V</i> , Å ³	5158(3)
<i>Z</i>	4
<i>D</i> _{calcd} , g cm ⁻³	1.607
<i>F</i> (000)	2488
Measurement of Intensity Data	
diffractometer	Philips PW1100
radiation (monochrom)	Cu Kα, 1.5418 Å (graphite)
scan rate, deg min ⁻¹	3–5.4
scan width, deg	1.2 + 0.15 tan θ
2θ range, deg	5–110
data collected	–16 ≤ <i>h</i> ≤ 16, 0 ≤ <i>k</i> ≤ 20, 0 ≤ <i>l</i> ≤ 18
no. of data collected	6802
no. of unique data	6486
no. of params varied	374
μ(Cu Kα), mm ⁻¹	9.213
<i>R</i> 1 [<i>I</i> > 2σ(<i>I</i>)]	0.081
wR2	0.19
goodness of fit on <i>F</i> ²	1.072

tion correction was applied via ψ scan with transmission factors in the range 1.001–1.46.²⁷ The computational work was carried out by intensively using the program SHELXL93.²⁸ Crystallographic details are reported in Table 1. The structure was solved by direct methods using the SIR92 program,²⁹ and all of the non-hydrogen atoms were found through a series of *F*_o Fourier maps. A CH₂Cl₂ solvent molecule was also introduced, although it was affected by some disorder. Non-metal-bound hydrogen atoms were introduced at calculated positions at a late stage of refinement. The latter was carried out by full-matrix least-squares calculations, initially with isotropic thermal parameters. In the last least-squares cycles anisotropic thermal parameters were used for the Rh, W, S, and P atoms and also for the C atoms, except for those of the P phenyl substituents and the CO molecules. In the last stage of refinement a peak of 0.9 e/Å³ was detected in the Δ*F* map corresponding to the expected bridging hydride ligand, and it was successfully refined.

No evidence whatsoever was found for the terminal H ligand. In the final Δ*F* maps significant peaks were found close to the heavy metal (largest value ca. 1.2 e/Å³), and were considered as ripples of no chemical relevance.

Results

Synthesis and Characterization of the Heterobimetallic Complex (triphos)Rh[*η*³-(CO)₅WS(C₆H₄)-CH=CH₂] (2**).** Complex **2** was straightforwardly prepared by electrophilic addition of the unsaturated fragment W(CO)₅ to the sulfur atom of the 2-vinylthiophenolate complex (triphos)Rh[*η*³-S(C₆H₄)CH=CH₂] (**1**), obtained by regioselective insertion of rhodium into the C₂–S bond of benzo[*b*]thiophene (BT) (Scheme 2).^{15b}

Compound **2** is stable in both the solid state and deaerated THF solutions, in which it does not decom-

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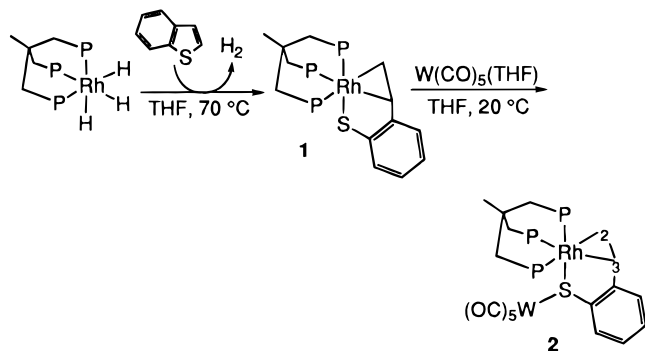
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Scheme 2



pose even at reflux temperature. In line with the structural formulation given in Scheme 2, the IR spectrum of **2** (Nujol mull or CH_2Cl_2 solution) in the ν -(C–O) region is characterized by four bands ($A_1^{(2)}$, B_1 , E , $A_1^{(1)}$), a pattern which is typical of $\text{W}(\text{CO})_5\text{L}$ complexes where L may be a unidentate thiolate ligand.³⁰ The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum features an AMQX pattern and is thus consistent with the magnetic inequivalence of the three phosphorus atoms of triphos. On the basis of NOESY studies on the related complex *exo*-[(triphos)- $\text{Ir}(\eta^3(\text{S}, \text{C}, \text{C})\text{-S}(\text{C}_6\text{H}_4)\text{CH}=\text{C}(\text{H})\text{Me})]$, obtained by insertion of the [(triphos)IrH] fragment into 2-methylbenzothiophene,³¹ the lowest field resonance (30.9 ppm) can be assigned to the P nucleus trans to the sulfur atom. The phosphorus chemical shifts do not significantly diverge from those of the thiolate precursor **1**, though one may notice a small high-field shift of the resonances pertaining to P_M and P_Q . This shielding effect may be due to the decreased electron density at the metal center in consequence of the electrophilic attack by the $\text{W}(\text{CO})_5$ group at the sulfur atom. A slight decrease of the metal basicity in the heterobimetallic complex (with consequent decrease of the metal π -back-bonding contribution to the $\text{M}-(\text{CH}=\text{CH}_2)$ bond) may be inferred also from the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, in which the H_2 and H_2' protons and the C_2 atom are shifted to lower field relative to the precursor **1**. In the latter compound both theoretical and reactivity studies agree that C_2 is a strong nucleophilic site in competition with the sulfur atom for binding electrophiles.^{15b} Accordingly, the C_2 carbon and its hydrogen atoms would be particularly sensitive to any alteration of the metal basicity, as is the case when a thiolate sulfur is replaced by a thioether sulfur. In conclusion, the NMR studies suggest that the bonding structure of the $\text{Rh}-(\text{CH}=\text{CH}_2)$ moiety acquires a less pronounced metallacyclopropane character in **2** as compared to **1**.

Carbonylation Reaction of 2. Besides its effects on the NMR parameters, the attack of $\text{W}(\text{CO})_5$ at the sulfur atom of the C–S-inserted BT in **2** has remarkable chemical implications due to the weakening of the bonding interaction between the metal center and the 2-vinylthiophenolate ligand. In fact, unlike **1**, the heterobimetallic complex **2** reacts with a relatively high pressure of CO (30 atm) even at room temperature, yielding a 3:3:1 mixture of **1**, $\text{W}(\text{CO})_6$, and [(triphos)-

$\text{Rh}(\text{CO})_2][(\text{CO})_5\text{W}(\text{o-S}(\text{C}_6\text{H}_4)\text{CH}=\text{CH}_2)]$ (**3**), in which the Rh and W centers belong to two distinct mononuclear complex species (Scheme 3).

Compound **3** was successfully separated from **1** and $\text{W}(\text{CO})_6$ by column chromatography and authenticated by NMR and IR spectroscopic techniques as well as by a sequence of reactions that unambiguously demonstrated the presence of a 2-vinylthiophenolate ligand exclusively bound to tungsten. Of crucial importance was the reaction of isolated **3** with $[\text{NBu}_4]\text{I}$ in THF, yielding the neutral complex (triphos) $\text{Rh}(\text{CO})\text{I}^{21}$ and $[\text{NBu}_4][(\text{CO})_5\text{W}(\text{o-S}(\text{C}_6\text{H}_4)\text{CH}=\text{CH}_2)]$ (**4**), which were separated from each other by chromatography. Finally, a pure sample of **4**, dissolved in THF, was treated with MeI to give $[\text{W}(\text{CO})_5\text{I}][\text{NBu}_4]$ ³² and free *o*-methylthiostyrene.^{15b,22}

The complex anion in **3** and **4** belongs to a family of numerous group 6 metal thiolates with the general formula $[\text{M}(\text{CO})_5\text{SR}]^-$.³⁰ Thus, a detailed description of the chemical–physical properties of the anion $[(\text{CO})_5\text{W}(\text{o-S}(\text{C}_6\text{H}_4)\text{CH}=\text{CH}_2)]^-$ is not warranted here. The only unprecedented NMR features pertain to the η^1 -thiolate ligand bound to tungsten, particularly the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR resonances of the hydrogen and carbon nuclei of the vinyl moiety. The chemical shifts and coupling constants are typical of such groups, however (*e.g.* the proton spectrum of **4** shows an upfield resonance at 7.13 due to H_3 , which is trans ($J(\text{H}_3\text{H}_{2\text{trans}}) = 17.5$ Hz) and cis ($J(\text{H}_3\text{H}_{2\text{cis}}) = 11.0$ Hz) to the gem hydrogens of C_2 at 5.69 and 5.30 ppm, respectively).

Hydrogenation Reactions of 2. In Situ HPNMR Study. When a THF- d_8 solution of **2** was pressurized with 30 atm of H_2 in a sapphire HPNMR tube, $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy showed, even at room temperature, the slow transformation of the starting W/Rh complex into a different dimeric species with the formula (triphos) $\text{RhH}(\mu\text{-H})[\mu\text{-o-S}(\text{C}_6\text{H}_4)\text{C}_2\text{H}_5]\text{W}(\text{CO})_4$ (**5**). Since the conversion is very slow at room temperature (20% in 3 days), the probe head of the spectrometer was heated to 70 °C. At this temperature, all **2** disappeared in 2 h, yielding **5** (Scheme 4).

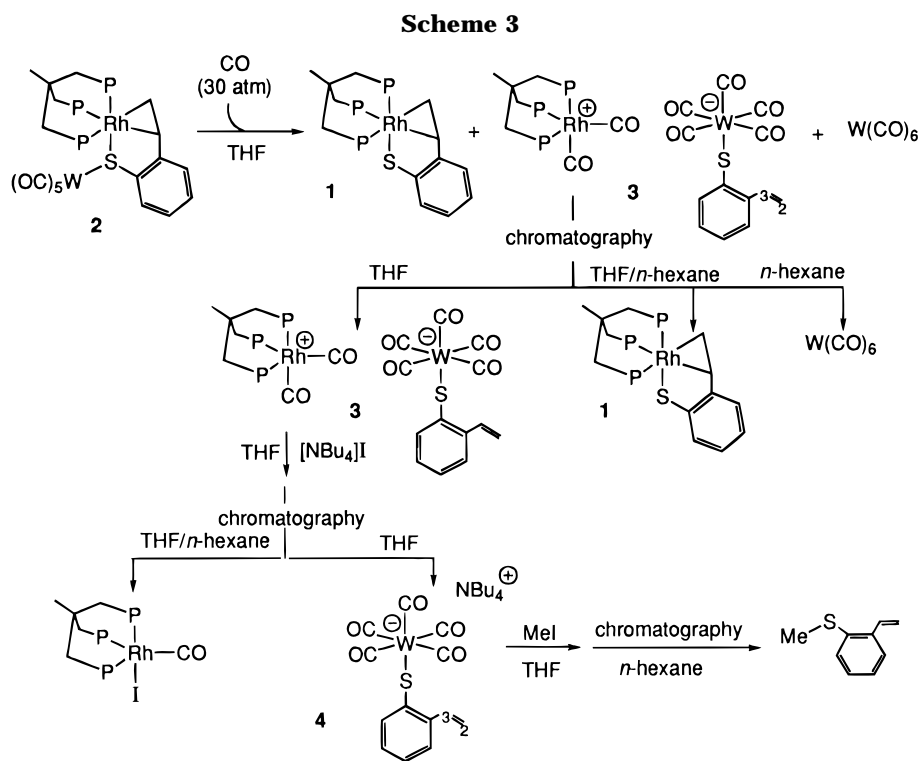
As shown by a variable-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR study, the conversion of **2** to **5** proceeds with no detectable intermediates. Even at 80 °C, however, **5** started disappearing. Formed in its place was the rhodium carbonyl complex (triphos) $\text{RhH}(\text{CO})$ (**6**). Increasing the temperature to 120 °C led to complete transformation of **5** into **6** in ca. 1 h, but the reaction was less selective, yielding a minor amount of the rhodium byproduct (triphos) $\text{Rh}(\text{CO})[\text{o-S}(\text{C}_6\text{H}_4)\text{C}_2\text{H}_5]$ (**7**).^{6d} A sequence of $^{31}\text{P}\{^1\text{H}\}$ NMR spectra illustrating these experiments is reported in Figure 1. After the HPNMR tube was depressurized, the contents were analyzed by GC/MS, showing the almost quantitative formation of ethylbenzene (EB) and traces of $\text{W}(\text{CO})_6$. A black, insoluble material analyzed as WS_x ($x_{\text{av}} = 1.5$ over five preparative reactions; see below) was also formed.

Isolation and Characterization of the Hydrogenation Intermediate 5. Having observed that the intermediate species **5** is stable in THF solution below 80 °C, a preparative-scale hydrogenation reaction of **2** was carried out using 30 atm of H_2 and a constant temperature of 70 °C. Workup of the reaction mixture

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gave brick red crystals of **5**, which were recrystallized from dichloromethane/ethanol to give $5 \cdot \text{CH}_2\text{Cl}_2$. An X-ray analysis was carried out on a single crystal (Figure 2). Crystallographic data and selected bond distances and angles for $5 \cdot \text{CH}_2\text{Cl}_2$ are listed in Tables 1 and 2, respectively.

As is evident from the ZORTEP drawing shown in Figure 2, the two formal d^6 metal centers (W^0 and Rh^{III}) appear as the central atoms of two octahedra sharing two basal sites, namely the bridging 2-ethylthiophenolate and hydride ligands. The hydride ligand with its two electrons cannot saturate the metals, however. In terms of the effective atomic number (EAN) rule, the total electron count of 34 implies the presence of a metal–metal bond, which in fact is found experimentally (e.g. the Rh–W distance is 3.06 Å, while the W–H_b–Rh angle is 134°). The electronic situation closely resembles that of the $[\text{M}(\text{CO})_5(\mu\text{-SH})]^-$ anions (M = Cr, W), comprising two isoelectronic terminal ML_5 fragments and a bent M–H_b–M bridge where the three-center–two-electron bond involves the formally empty σ -hybrid orbitals of the two ML_5 fragments and the filled H_{1s} orbital.³³ The C–C bond lengths in the organic substituent of the thiophenolate ligand confirm that hydrogenation of the vinyl double bond has occurred with formation of an ethyl group. Unlike the bridging

hydride H_b, the terminal hydride H_t was not located, although its position trans to P1 may be inferred from the long P1–Rh distance (2.414(4) vs 2.293(4) Å (average) of Rh–P2,3) that correlates with the great trans influence of the hydride ligand. The presence of a terminal hydride ligand bound to rhodium and the overall solid-state structure of **5** are totally consistent with the IR ($\nu(\text{Rh-H})$ 1996 cm^{-1}) and NMR data for the complex in solution. At room temperature, the $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum consists of a canonical AMQX pattern, the P_M and P_Q components of which significantly broaden, losing their multiplicity at higher temperature (Figure 3). A slow exchange of the terminal and bridging hydride ligands (H_b, δ –9.88, $J(\text{H}_b\text{Rh})$ = 19.02 Hz, $J(\text{H}_b\text{H}_t)$ = 5.45 Hz, $J(\text{H}_b\text{P}_M)$ = 100.6 Hz, $J(\text{H}_b\text{W})$ = 34.2 Hz; H_t, δ –10.07, $J(\text{H}_t\text{Rh})$ = 6.76 Hz, $J(\text{H}_t\text{P}_Q)$ = 181.5 Hz) may well account for the slight fluxionality exhibited by their trans phosphorus atoms.

Desulfurization of the 2-Ethylthiophenolate Ligand. In Situ and Batch Reactions. Heating to 120 °C for 3 h a HPNMR tube containing a THF-*d*₈ solution of pure **5** under 30 atm of H₂ resulted in the transformation of the heterobimetallic dimer into the carbonyl hydride complex **6**, EB, and “WS_x”. No intermediate species was seen by variable-temperature ^1H and ^{31}P NMR spectroscopy along this transformation, which occurred even above 70 °C. In the absence of added H₂, the desulfurization of the bridging thiolate to give **6**, EB, and WS_x still occurred by thermolysis of

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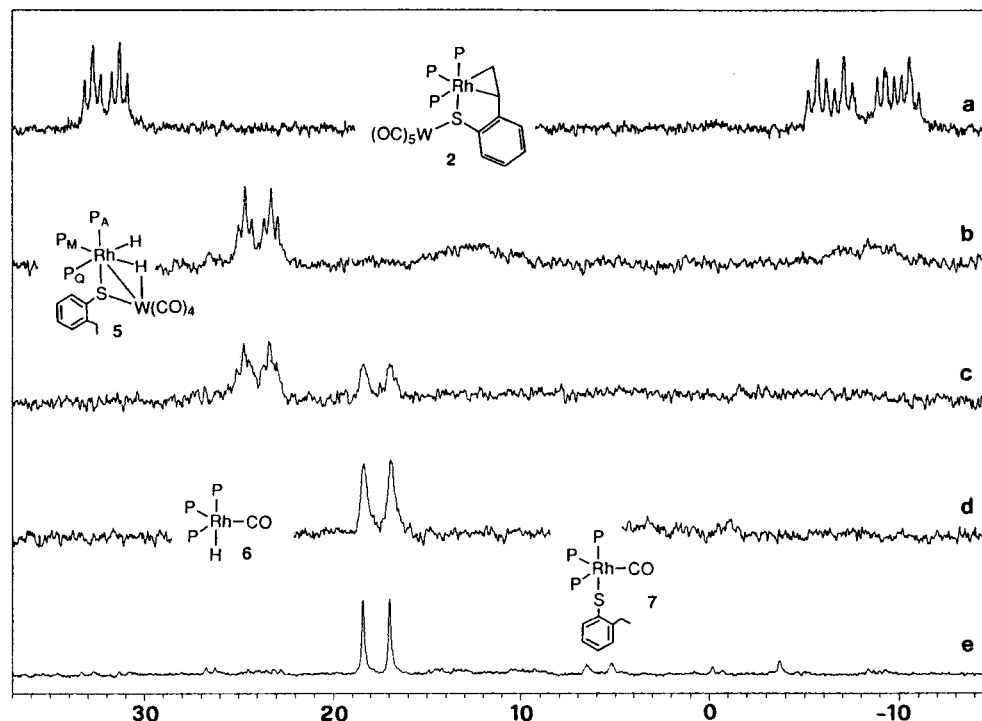


Figure 1. $^{31}\text{P}\{^1\text{H}\}$ HPNMR study (sapphire tube, $\text{THF-}d_8$, 81.01 MHz) of the reaction of **2** with hydrogen (30 atm): (a) at room temperature; (b) after 2 h at 70 °C; (c) after the probe was heated to 100 °C for 1 h; (d) after further heating to 120 °C for 1 h; (e) after the NMR probe was cooled to room temperature.

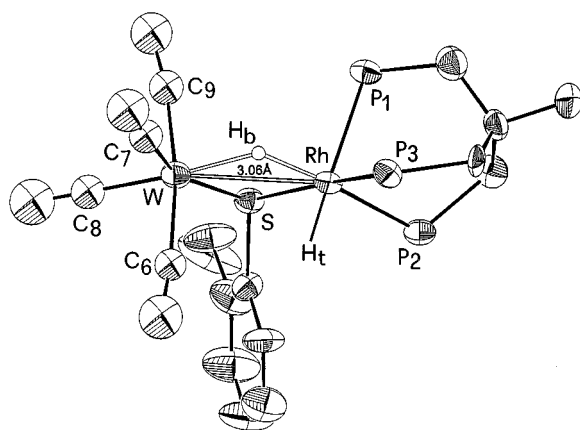


Figure 2. ZORTEP drawing of the binuclear compound [(triphos)RhH(μ -H){ μ -*o*-S(C₆H₄)C₂H₅}W(CO)₄] in **5**·CH₂Cl₂. Phenyl rings of triphos are omitted for clarity. The atom H_t could not be located by normal X-ray procedures, and it is shown at the vacant octahedral site about the rhodium atom.

5 in THF. The reaction, however, was less selective as appreciable amounts of the carbonyl thiolate complex **7** and of other unidentified species were also formed. Preparative-scale hydrogenations of **5**, carried out in an autoclave at 120 °C and with 30 atm of H₂, gave sufficient amounts of WS_x for analytical purposes.

In Situ Preparation of [W(CO)₅(*o*-S(C₆H₄)C₂H₅)]⁻ and Its Reaction with H₂. A 10 mm sapphire HPNMR tube containing a THF-*d*₈ solution of **5** was pressurized with 30 atm of CO at room temperature (Scheme 5). Even already at 40 °C, a reaction occurred that converted all the heterobimetallic Rh/W complex into two mononuclear species: the cation [(triphos)Rh(CO)₂]⁺ and the anion [W(CO)₅(*o*-S(C₆H₄)C₂H₅)]⁻. The evolution of free H₂ was also observed by ¹H NMR spectroscopy. After CO was replaced by H₂ (30 atm),

Table 2. Selected Bond Distances (Å) and Angles (deg) for **5**·CH₂Cl₂

Distances			
W(1)–C(8)	1.88(2)	W(1)–H _b	1.75(16)
W(1)–C(9)	1.95(2)	Rh(1)–P(3)	2.282(4)
W(1)–C(7)	1.94(2)	Rh(1)–P(2)	2.314(4)
W(1)–C(6)	1.96(2)	Rh(1)–S(1)	2.407(4)
W(1)–S(1)	2.493(4)	Rh(1)–P(1)	2.414(4)
W(1)–Rh(1)	3.0554(14)	Rh(1)–H _b	1.57(16)
Angles			
C(8)–W(1)–C(9)	86.5(7)	C(8)–W(1)–H _b	172(5)
C(8)–W(1)–C(7)	91.4(7)	P(3)–Rh(1)–P(2)	89.11(14)
C(9)–W(1)–C(7)	88.4(7)	P(3)–Rh(1)–S(1)	169.89(14)
C(8)–W(1)–C(6)	84.4(7)	P(2)–Rh(1)–S(1)	97.50(14)
C(9)–W(1)–C(6)	170.8(7)	P(3)–Rh(1)–P(1)	88.63(14)
C(7)–W(1)–C(6)	90.3(7)	P(2)–Rh(1)–P(1)	92.34(14)
C(8)–W(1)–S(1)	107.5(6)	S(1)–Rh(1)–P(1)	98.68(13)
C(9)–W(1)–S(1)	85.7(5)	P(3)–Rh(1)–W(1)	118.65(11)
C(7)–W(1)–S(1)	159.8(5)	P(2)–Rh(1)–W(1)	146.62(11)
C(6)–W(1)–S(1)	98.5(5)	S(1)–Rh(1)–W(1)	52.70(9)
C(8)–W(1)–Rh(1)	156.4(5)	P(1)–Rh(1)–W(1)	105.59(10)
C(9)–W(1)–Rh(1)	97.8(5)	P(2)–Rh(1)–H _b	170(5)
C(7)–W(1)–Rh(1)	111.9(5)	Rh(1)–S(1)–W(1)	77.14(11)
C(6)–W(1)–Rh(1)	91.1(5)	W(1)–H _b –Rh(1)	134(3)
S(1)–W(1)–Rh(1)	50.16(9)		

no appreciable reaction occurred below 70 °C. At this temperature, however, ETP began to form slowly with concomitant degradation of [W(CO)₅(*o*-S(C₆H₄)C₂H₅)]⁻, while the dicarbonyl complex [(triphos)Rh(CO)₂]⁺ was apparently stable. After 1 h at 70 °C, the production of free ETP was practically quantitative, as shown by GC/MS. W(CO)₆ was the only tungsten complex detected, while no production of EB was observed.

Attempted HDS of BT by Molybdenum or Tungsten Mononuclear Complexes. Various mononuclear complexes containing metals belonging to the class of HDS components have been employed as precursors for the hydrogenation (30 atm of H₂) of BT in THF. All of the compounds investigated, (triphos)WH₆ (**9**),¹⁷ (triphos)Mo(η^6 -C₆H₆) (**10**),²³ [(triphos)MoH(η^6 -C₆H₆)]BF₄

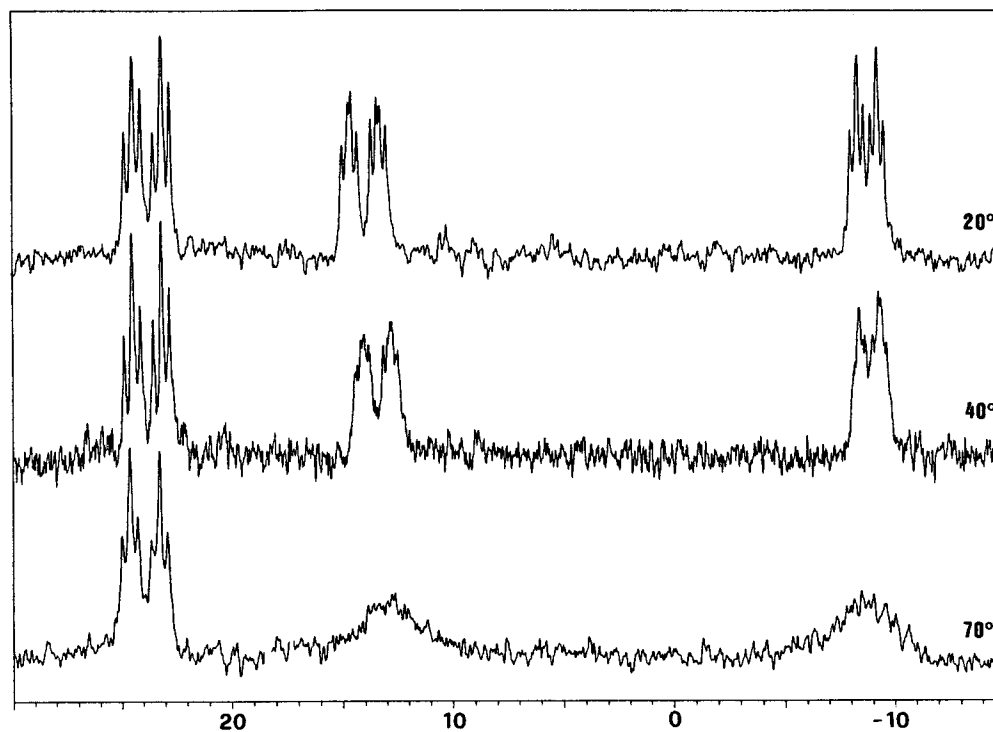
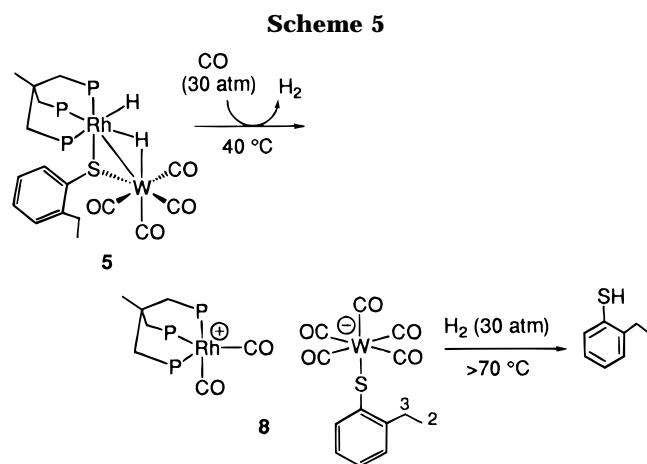
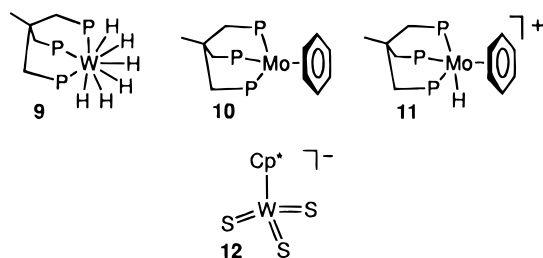


Figure 3. Variable-temperature (°C) $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (sapphire tube, $\text{THF-}d_6$, 81.01 MHz) of **5**.



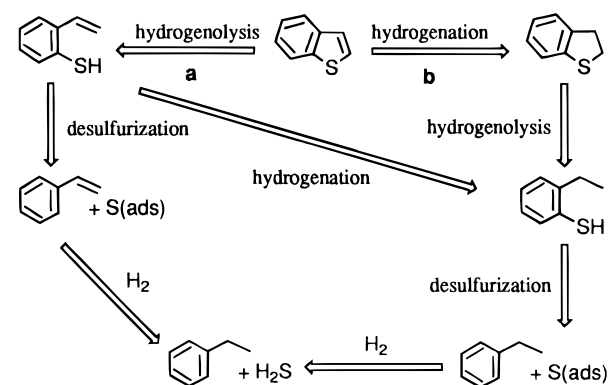
(11),²³ $[\text{Cp}^*\text{WS}_3](\text{PPh}_4)$ **(12)**,²⁴ $\text{W}(\text{CO})_6$, and $\text{W}(\text{CO})_5\text{THF}$, did not catalyze any transformation of BT even under forcing conditions (160–200 °C, 30 atm of H_2).



Discussion

From a mechanistic viewpoint, the heterogeneous HDS of thiophenes is a very complicated process that depends critically on many factors, among which important roles are played by the structure and the molecular size of the substrate and by the structure and the composition of the catalyst.^{3,4} For BT, either hydrogenolysis or hydrogenation reactions have been

Scheme 6. Proposed Reaction Pathways for the HDS Reaction of Benzo[*b*]thiophene



considered as the initial steps of alternative pathways leading to EB and H_2S (Scheme 6).

In spite of extensive research on promoted Mo or W catalysts, the chemical role of the promoter metal atom in the HDS of BT is practically unknown. In analogy to the model proposed by Topsøe^{3a} and Startsev^{4a} for thiophene HDS on Co–Mo–S catalysts, it is possible that BT is preferentially adsorbed on coordination vacancies associated with the promoter atoms, while hydrogen is activated on MoS_2 (WS_2) edge sites. In this eventuality, the following transfer of hydrogen atoms (most likely from $\text{Mo(W)}\text{-SH}$ groups) to the adsorbed BT would result in either hydrogenolysis or hydrogenation reactions, depending on the type of activation undergone by the substrate, *i.e.* C–S insertion (hydrogenolysis to thiol) or coordination in the intact form (hydrogenation to DHBT).

The results presented in this work show that the C–S opening of BT readily occurs at a promoter metal (Rh) but the desulfurization of the hydrogenolysis thiolate product requires the aid of a component metal (W) to take place under very mild reaction conditions. It is just the component metal that ultimately traps the ex-

truded sulfur atom. The desulfurization of the thiolate to EB proceeds through a Rh/W dimeric intermediate in which the metal centers are held together by bridging 2-ethylthiophenolate and hydride ligands and occurs thermally (>70 °C) with no need of external hydrogen (an excess of the latter reagent helps to minimize the side reaction leading to the formation of the thiolate carbonyl complex **7**, however).

The homogeneous HDS of BT has recently been observed by other groups.^{10a,11} Among the known examples, that described by Vicic and Jones shows differences but also interesting analogies to ours (Scheme 1). The reaction assisted by the homometallic dimer [Cp*IrHCl]₂ is apparently intermolecular, as it requires the addition of H₂ and also needs a high temperature (150 °C) to take place. Moreover, the fate of the sulfur was not determined. Nevertheless, like **5**, the intermediate that precedes the S–C(aryl) bond cleavage contains a μ -thiolato bridge. This leads us to believe that the multipoint coordination of the RS[–] groups (particularly when they simultaneously bridge promoter and component metals) may be very important in bringing about the C–S bond scission. Indeed, as recently demonstrated by Curtis and Druker,¹⁴ arene thiols (the products of the hydrogenolysis of the benzothiophenes) are easily desulfurized by the cluster Cp₂Mo₂Co₂S₃(CO)₄ with a mechanism in which the C–S bond of μ_3 -SR groups is homolytically cleaved. The bridging bonding mode of the thiolato ligands was proposed to be the factor that drastically reduces the C–S bond dissociation energy.

The increase in HDS activity of promoted heterogeneous catalysts has also been correlated to the higher mobility of the surface S atoms.¹⁴ Curtis and Druker have recently interpreted the fluxionality of certain intermediates that precede the desulfurization of thiols with Cp₂Mo₂Co₂S₃(CO)₄ in terms of a facile movement of RS[–] groups over the face of the cluster. The concept of *latent vacancies* was applied to define the Co atoms from which the thiolate groups move to bind neighboring Mo atoms. In this work, we have shown that 2-vinylthiophenolate and 2-ethylthiophenolate groups can easily move from the promoter (responsible for the hydrogenolysis of BT) to the component (responsible for the following desulfurization step) (Schemes 3 and 5). When, however, the thiolate is exclusively bound to W as in **8**, its desulfurization by action of H₂ does not occur in the conditions employed for the desulfurization of the heterobimetallic complex **5**. The concomitant presence of promoter and component metals thus seems important in order to have the HDS of BT through the mechanism that begins with the hydrogenolysis reaction (Scheme 6, path **a**). On the other hand, the key role of the metal promoter in the hydrogenolysis of thiophenes is supported by several homogeneous modeling studies, which clearly show that C–S bond scission is almost exclusively brought about by promoter metal complexes.⁵ Consistently, we have found that various W or Mo complexes do not catalyze any transformation of BT under the reaction conditions that are currently employed with hydrogenation or hydrogenolysis catalysts containing promoter metal complexes.^{5b}

It is generally observed that both the C–S opening of thiophenes by metal promoters⁵ and the desulfurization of thiols by metal components^{14,34} are low-energy processes in the homogeneous phase (as shown in this paper, both reactions take place even at 70 °C). In contrast, the removal of sulfur from complexes containing metal-sulfur multiple bonds by reaction with H₂ is a very difficult process, uniquely observed for Cp*₂Ti(S)py (py = pyridine).³⁵ For example, Cp*WCl₄ desulfurizes at low temperature the dithiolate SCH₂CH₂S^{2–} to give [Cp*WS₃][–],²⁴ which is stable in THF at 160 °C under 30 atm of H₂. Only by addition of a strong acid does the hydrogenation of [Cp*WS₃][–] cause the evolution of H₂S. Once again, results of homogeneous modeling studies have implications for the heterogeneous HDS of thiophenes. It has been proposed, in fact, that the rate-determining step on real catalysts is the removal of surface sulfur (as H₂S) and not substrate adsorption, C–S insertion, or C–S cleavage.³⁴

Conclusions

The aim of this work was to tackle some questions regarding the HDS mechanism of thiophenes, particularly the specific role played by metals belonging to the classes of the promoters (Rh) and of the components (W) in the degradation of benzo[*b*]thiophene to ethylbenzene and “S” or H₂S. It has been shown that the hydrogenolysis of benzo[*b*]thiophene to 2-vinylthiophenol or 2-ethylthiophenol is a facile process for the promoter, but the desulfurization step needs the assistance of a component metal to take place. It has also been found that the desulfurization of the 2-ethylthiophenolate ligand is favored when it bridges the Rh and W centers.

Given the complexity of the heterogeneous HDS reaction and the many possible mechanisms that may be operative even on the surface of the same catalyst, our results must be considered with extreme caution. Many of them, however, show a surprising consistency with related reactions occurring over the surface of Co/Mo/S phase catalysts.

Acknowledgment. Thanks are due to Professors M. T. Ashby and K. Tatsumi for loans of (triphos)Mo(η^6 -C₆H₆) and [Cp*WS₃](PPh₄), respectively. The contributions of the CNR (Italy) and CONICIT (Venezuela) research programs are also acknowledged.

Supporting Information Available: Tables of bond distances and angles (Table S1), final coordinates with equivalent isotropic thermal parameters (Table S2), anisotropic thermal parameters (Table S3), and atomic coordinates of the hydrogen atoms (Table S4) for **5**·CH₂Cl₂ (8 pages). Ordering information is given on any current masthead page.

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