Opening and Hydrogenation of Dinaphtho[2,1-*b*:1′,2′-*d*]thiophene (DNT) by Soluble Rhodium and Iridium Complexes. Homogeneous Hydrogenolysis of DNT to 1,1′-Binaphthalene-2-thiol by Rhodium Catalysis

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The fragment [(triphos)IrH], generated *in situ* by thermolysis of (triphos)Ir(H)$_2$(C$_2$H$_5$) in THF, reacts with dinaphtho[2,1-*b*:1′,2′-*d*]thiophene (DNT) at temperatures higher than 100 °C to give a temperature-invariant 3:2 mixture of the two diastereomeric C−S insertion products (triphos)IrH(η^2(*C*,*S*)-C$_{20}$H$_{12}$S) (**3a**,**b**; triphos = MeC(CH$_2$PPh$_2$)$_3$). In the temperature range from 70 to 100 °C, the reaction gives kinetic mixtures of the C−S insertion products and of the complex (triphos)IrH(η^2-C$_{20}$H$_{12}$S) (**2**), which is suggested to contain an intact DNT molecule bound to iridium *via* a double bond from a naphthyl ring. Complex **2** in THF transforms into **3a**,**b** even at 70 °C. Hydrogenation of **3a**,**b** (30 atm of H$_2$, 60 °C) in THF gives the dihydride thiolate complex (triphos)Ir(H)$_2$(SC$_{20}$H$_{13}$), which is protonated by strong acids, converting to the dimer [(triphos)IrH(μ-SC$_{20}$H$_{13}$)$_2$HIr(triphos)](BPh$_4$)$_2$. The latter compound is straightforwardly obtained by reaction of **3a**,**b** with protic acids. The complex (triphos)RhH$_3$ (**6**) reacts with DNT (THF, 70 °C) to give exclusively the dihydride thiolate product (triphos)Rh(H)$_2$(SC$_{20}$H$_{13}$). The latter complex reacts in THF with KOBu^t in the presence of H$_2$ (5 atm) at room temperature to give the trihydride **6** and potassium 1,1′-binaphthalene-2-thiolate. In the presence of a strong base (KOBu^t), the π-alkyne complex [(triphos)Rh(η^2-MeO$_2$CC≡CCO$_2$Me)]PF$_6$ in THF behaves as a catalyst precursor for the homogeneous hydrogenolysis of DNT to 1,1′-binaphthalene-2-thiol (30 atm of H$_2$, 160 °C). In the proposed mechanism, the [(triphos)RhH] fragment acts as the catalyst while the added base plays a dual role: it serves to generate the catalyst from the precursor and accelerates the reaction rate by influencing the rate-determining step positively.

Introduction

In very heavy oils, polyalkylated thiophenes and fused-ring thiophenes constitute the majority of sulfur-containing species (Figure 1) and the substrates which are most difficult to degrade under hydrodesulfurization (HDS) conditions.[2,3]

In contrast to studies under actual reactor conditions with industrial catalysts,[3a,b] modeling studies of the reactions between soluble metal complexes and higher ring systems than dibenzo[*b*,*d*]thiophene are absent in the relevant literature.[4]

In earlier work, we have shown that the 16-electron systems [(triphos)MH] (M = Rh,[5] Ir;[6] triphos = MeC(CH$_2$PPh$_2$)$_3$), generated *in situ* by thermolysis of appropriate 18-electron precursors in THF, react with thiophene (T), benzo[*b*]thiophene (BT), and dibenzo[*b*,*d*]thiophene (DBT) to give stable C−S insertion products (Scheme 1).[7]

Irrespective of the final structure of the C−S insertion product, all the reactions illustrated in Scheme 1 proceed through the intermediacy of isolable kinetic (hydrido)metallathiacycles having the structure of the iridadibenzothiabenzene complex (Scheme 1). From

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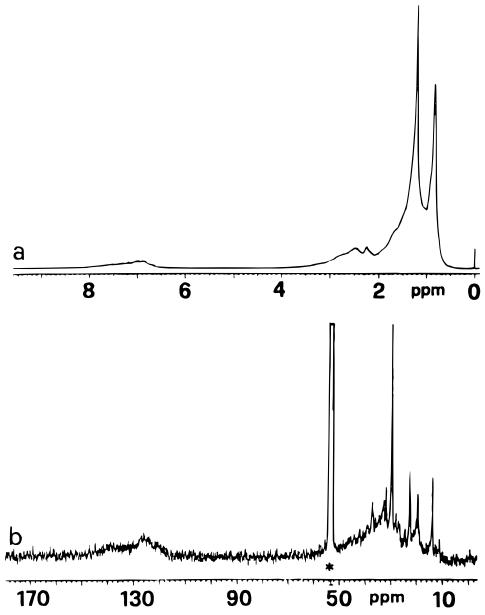
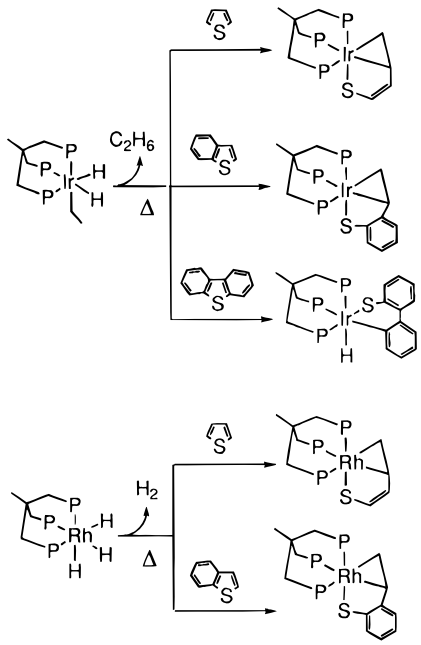


Figure 1. (a) ^1H ($CDCl_3$) and (b) $^{13}C\{^1H\}$ NMR (CD_2Cl_2; the asterisk denotes the solvent resonance) spectra of "Cerro Negro" crude oil. Source: INTEVEP SA, Los Teques, Venezuela.

Scheme 1



this study, it was concluded that the energy barrier to C−S insertion increases in the order T ≤ BT < DBT.[7]

In this paper, we describe the reactions between the [(triphos)MH] fragments and dinaphtho[2,1-*b*:1′,2′-*d*]-thiophene (DNT), which is an actual contaminant in oil,[2a] and also report the first example of catalytic hydrogenolysis of DNT to 1,1′-binaphthalene-2-thiol.

Experimental Section

General Information. All reactions and manipulations were routinely performed under a nitrogen atmosphere by using standard Schlenk techniques. High-pressure, high-temperature reactions under controlled pressure of hydrogen were performed with a stainless steel Parr 4565 reactor equipped with a Parr 4842 temperature and pressure controller. Tetrahydrofuran (THF) was distilled from $LiAlH_4$, stored over molecular sieves, and purged with nitrogen prior to use. Potassium *tert*-butoxide ($KOBu^t$, 95%) was purchased from Aldrich and used without further purification. All other chemicals were commercial products and were used as received without further purification. Dinaphtho[2,1-*b*:1′,2′-*d*]thiophene (DNT) was prepared by a literature method.[8] Starting materials (triphos)$Ir(H)_2(C_2H_5)$,[9] (triphos)$Rh(H)_3$,[5b] and [(triphos)Rh-(η^2-$MeO_2CC{\equiv}CCO_2Me$)]PF_6[10] were prepared as previously described. Deuterated solvents for NMR measurements were dried over molecular sieves. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were obtained on either a Bruker ACP 200 (200.13, 50.32, and 81.01 MHz, respectively) or a Varian VXR 300 (299.94, 75.43, and 121.42 MHz, respectively) spectrometer. All chemical shifts are reported in 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. The computer simulation of NMR spectra was carried out with a locally developed package containing the programs LAOCN3[11] and Davins[12] 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. The 10 mm sapphire NMR tube was purchased from Saphikon, Milford, NH, while the titanium high-pressure charging head was constructed at ISSECC-CNR (Firenze, Italy). Conductivities were measured with an Orion Model 990101 conductance cell connected to a Model 101 conductivity meter. The conductivity data were obtained at sample concentrations of ca. 10^{-3} M in nitroethane solutions at room temperature. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrophotometer using samples mulled in Nujol between KBr plates. 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.

Reaction of (triphos)$Ir(H)_2(C_2H_5)$ (1) with DNT. A. NMR Experiment. A sample of **1** (30 mg, 0.035 mmol) together with a 4-fold excess of DNT (40 mg, 0.14 mmol) were dissolved in THF-d_8 (0.8 mL), and this solution was then transferred into a 5 mm NMR tube under nitrogen. After two freeze/pump/thaw cycles at −196 °C, the tube was flame-sealed and then placed into an oil bath preheated to 70 °C. After 2 h, the tube was cooled to room temperature and $^{31}P\{^1H\}$ and ^1H NMR spectra were recorded at room temperature. In addition to the starting complex **1** (70%), three other products (**2**, **3a**, and **3b**) were observed in a ratio of 50:31:19 on the basis of ^{31}P integration. Compounds **3a** and **3b** were unambiguously identified as diastereomeric C−S insertion products of the formula (triphos)IrH(η^2(*C*,*S*)-$C_{20}H_{12}S$) by comparison with authentic samples (see below). On the basis of the $^{31}P\{^1H\}$ NMR AMQ pattern and of hydride and olefinic resonances in the ^1H NMR spectrum (see below), we assigned **2** as (triphos)IrH(η^2-$C_{20}H_{12}S$), in which an intact DNT molecule binds the metal in an η^2 mode *via* a C−C bond from one of the two naphthyl rings (most likely the C_6−C_{6a} carbon atoms; *vide*

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infra).[13] The tube was then kept at 70 °C in an oil bath for several 2 h periods, and NMR spectra were recorded after every period; during this time, **1** was gradually consumed, while **2** converted to **3a** and **3b**. After ca. 24 h, 60% conversion of **1** was achieved with the following product distribution: **2** (37%), **3a** (39%), and **3b** (24%). The tube was then placed into an oil bath preheated to 100 °C. After 4 h at this temperature, $^{31}P\{^1H\}$ and ^1H NMR spectra, recorded at room temperature, showed an 80% conversion of **1** and a ratio between **3a** and **3b** of ca. 3:2. Compound **2** was detected only in traces. On the basis of this product distribution, one may easily infer that, at 100 °C, the conversion of **2** to both **3a** and **3b** proceeds more rapidly than the reaction of **1** with DNT. At 100 °C, complete conversion of **1** was achieved after a further 10 h with identical diastereomeric preference for **3a** (ratio of 3:2).

B. Synthesis of (triphos)IrH(η^2(*C,S*)-$C_{20}H_{12}S$) (Diastereomeric 3:2 Mixture of 3a and 3b). A Parr reactor was charged with a solid sample of **1** (0.20 g, 0.24 mmol) and a solution of DNT (0.27 g, 0.96 mmol) in THF (50 mL) under nitrogen at room temperature and then heated to 120 °C for 4 h. The reactor was cooled to room temperature, and the contents were transferred into a Schlenk-type flask. The volatiles were removed under vacuum, and the residue was characterized as a ca. 3:2 mixture of **3a** and **3b**. Recrystallization from CH_2Cl_2 and ethanol gave sandy white microcrystals which were collected by filtration and washed with *n*-pentane; yield 85%. The two diastereomers, in a 3:2 ratio, could not be separated by either recrystallization or liquid chromatography. No isomerization reaction occurred by heating solutions of the mixture of **3a** and **3b** in THF up to 160 °C for 2 h. Anal. Calcd (found) for $C_{61}H_{52}IrP_3S$: C, 66.47 (66.33); H, 4.75 (4.64); S, 2.91 (2.81). IR: ν(Ir−H) 2088 (m) cm^{-1}. Compound **3a**: $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C, 121.42 MHz) AMQ spin system, δ −8.59 (t, $J(P_AP_M) = J(P_AP_Q) =$ 14.4 Hz, P_A), −24.05 (dd, $J(P_MP_Q) = 16.8$ Hz, P_M), −49.89 (dd, P_Q); ^1H NMR (CD_2Cl_2, 20 °C, 299.94 MHz) δ −7.88 (dt, $J(HP_Q) = J(HP_A) = J(HP_M) = 11.8$ Hz, Ir−H); broad-band $^1H\{^{31}P\}$ NMR (CD_2Cl_2, 20 °C) δ −7.88 (s, Ir−H); $^{13}C\{^1H\}$ NMR (THF-d_8, 20 °C, 50.32 MHz) δ 168.3 (d, J(CP) = 4.4 Hz, Ir−C). Compound **3b**: $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C, 121.42 MHz) AMQ spin system, δ −8.59 (t, $J(P_AP_M) = 14.2$ Hz, $J(P_AP_Q) =$ 13.3 Hz, P_A), −24.26 (dd, $J(P_MP_Q) = 16.7$ Hz, P_M), −49.20 (dd, P_Q); ^1H NMR (CD_2Cl_2, 20 °C, 299.94 MHz) δ −7.83 (dt, $J(HP_Q) = 154.0$ Hz, $J(HP_A) = J(HP_M) = 11.5$ Hz, Ir−H); broad-band $^1H\{^{31}P\}$ NMR (CD_2Cl_2, 20 °C) δ −7.83 (s, Ir−H); $^{13}C\{^1H\}$ NMR (THF-d_8, 20 °C, 50.32 MHz) δ 168.8 (d, J(CP) = 4.2 Hz, Ir−C).

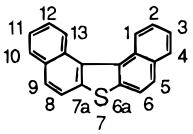
C. Synthesis of (triphos)IrH(η^2-$C_{20}H_{12}S$) (2). A Parr reactor was charged with a solid sample of **1** (0.20 g, 0.24 mmol) and a solution of DNT (0.27 g, 0.96 mmol) in THF (50 mL) under nitrogen at room temperature and then heated to 70 °C. After 24 h, the reactor was cooled to room temperature and the contents were transferred into a Schlenk-type flask. The volatiles were removed under vacuum, and the $^{31}P\{^1H\}$ NMR spectrum of the residue gave the following mixture composition: **1** (34%), **2** (27%), **3a** (24%), and **3b** (15%). Notwithstanding several attempts, we did not succeed into isolating a pure sample of **2** from the reaction mixture by either recrystallization or liquid chromatography. The $^{31}P\{^1H\}$ and ^1H NMR chemical shifts and coupling constants were thus obtained from samples of **2** invariably contaminated by **1**, **3a**, and **3b**. $^{31}P\{^1H\}$ NMR (THF-d_8, 20 °C, 81.01 MHz): AMQ pattern, δ −10.8 (dd, $J(P_AP_M) = 14.3$ Hz, $J(P_AP_Q) = 9.3$ Hz, P_A), −32.6 (t, $J(P_MP_Q) = 16.7$ Hz, P_M), −38.0 (dd, P_Q). ^1H NMR (THF-d_8, 20 °C, 200.13 MHz): δ −9.11 (ddd, $J(HP_{trans}) = 160.8$ Hz, $J(HP_{cis}) = 14.0$, 10.2 Hz, Ir−H), 5.78 (dd, J(HP) = 8.3 Hz, J(HH) = 7.4 Hz, C−H), 6.4 (masked by aromatic proton resonances, the correlation between this signal and that at 5.78 ppm was determined by a $^1H,^1H$ 2D-COSY experiment, C−H). Broad-band $^1H\{^{31}P\}$ NMR (THF-d_8, 20 °C, 200.13 MHz): δ −9.11 (s, Ir−H), 5.78 (d, J(HH) = 7.4 Hz, C−H), 6.4 (masked, C−H).

This reaction between **1** and DNT was repeated in a sapphire high-pressure NMR (HPNMR) tube. After 24 h at 70 °C, the tube was cooled down to room temperature and then analyzed by $^{31}P\{^1H\}$ NMR spectroscopy, which showed product distribution identical with that in the preparative-scale reaction. The tube was pressurized with 3 atm of CO and then was introduced into a NMR probe at 20 °C. Even the first $^{31}P\{^1H\}$ NMR spectrum showed the complete disappearance of **2**. Formed in its place was the known (triphos)IrH(CO) complex.[14]

Reaction of the Diastereomeric Mixture of 3a and 3b with H_2. Synthesis of (triphos)Ir(H)$_2$($SC_{20}H_{13}$) (4). A solution of a 3:2 mixture of **3a** and **3b** (0.20 g, 0.18 mmol) in THF (30 mL) was pressurized with hydrogen to 30 atm at room temperature in a Parr reactor and then heated to 100 °C for 2 h. The reactor was then cooled to room temperature; after it was depressurized and vented under a nitrogen stream, the contents were transferred into a Schlenk-type flask. Addition of *n*-heptane (40 mL) led to the precipitation of **4** as pale yellow crystals in almost quantitative yield. Anal. Calcd (found) for $C_{61}H_{54}IrP_3S$: C, 66.35 (66.01); H, 4.93 (4.87); S, 2.90 (2.79). IR: ν(Ir−H) 2071 (s), 2038 (sh) cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C, 81.01 MHz): AMQ spin system, δ −2.4 (t, $J(P_AP_M) = J(P_AP_Q) = 13.8$ Hz, P_A), −26.8 (t, $J(P_MP_Q) = 13.8$ Hz, P_M), −28.8 (t, P_Q). ^{31}P NMR (CD_2Cl_2, 20 °C, 81.01 MHz): δ −2.4 (br s, P_A), −26.8 (br d, $J(P_MH) =$ ca. 150 Hz, P_M), −28.8 (br d, $J(P_QH) =$ ca. 150 Hz, P_Q). ^1H NMR (CD_2Cl_2, 20 °C, 200.13 MHz): δ −9.2 (doublet of multiplets, $J(HP_{trans}) =$ ca. 150 Hz, 2H, Ir−H). Broad-band $^1H\{^{31}P\}$ NMR (CD_2Cl_2, 20 °C, 200.13 MHz): δ −9.23 ($J(H_AH_B) = 5.49$ Hz, Ir−H_A), −9.26 (Ir−H_B); these parameters have been used for the computer simulation of the hydride resonances (AB spin system) in the experimental spectrum. The reaction between the diastereomeric mixture of **3a** and **3b** and hydrogen was also carried out in an HPNMR tube under 30 atm of hydrogen pressure and was followed by ^1H and ^{31}P NMR spectroscopy. The reaction occurred even at ca. 60 °C. At 80 °C, all **3a** and **3b** were consumed in ca. 2 h to give **4** with no detection of intermediate species; during the course of the reaction the ratio between the two isomers **3a** and **3b** remained practically constant.

Reaction of the Diastereomeric Mixture of 3a and 3b with HBF_4·OEt_2. Synthesis of [(triphos)IrH(μ-$SC_{20}H_{13}$)$_2$HIr(triphos)](BPh_4)$_2$ (5). A slight excess of HBF_4·OEt_2 (40 mL, 0.20 mmol) was added to a solution of a 3:2 isomeric mixture of **3a** and **3b** (0.20 g, 0.18 mmol) in CH_2Cl_2 (20 mL) at room temperature. There was an immediate color change from pale yellow to red-orange. After ca. 20 min, $NaBPh_4$ (0.85 g, 0.25 mmol) in ethanol (30 mL) was added to the reaction mixture. On partial evaporation of the solvents under a brisk stream of nitrogen, red microcrystals of **5** precipitated. They were filtered off and washed with ethanol and *n*-pentane; yield 80%. Anal. Calcd (found) for $C_{170}H_{146}B_2Ir_2P_6S_2$: C, 71.77 (70.99); H, 5.17 (5.18); S, 2.25 (2.11). Λ_M: 102 Ω^{-1} cm^2 mol^{-1}. IR: ν(Ir−H) 2088 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR (THF-d_8, −30 °C, 81.01 MHz): ABM spin system, δ 10.5 (dd, $J(P_AP_B) = 42.3$ Hz, $J(P_AP_M) = 8.6$ Hz, P_A), 9.1 (dd, $J(P_BP_M) = 10.2$ Hz, P_B), 1.6 (t, P_M). ^1H NMR (THF-d_8, −30 °C, 200.13 MHz): δ −1.29 (dt, $J(HP_{trans}) = 131.6$, $J(HP_{cis}) = 10.1$ Hz, Ir−H). The reaction between **3a**,**b** and HBF_4·OEt_2 was repeated in a NMR tube in THF-d_8: again **5** was the only product detectable on the NMR

(13) Numbering scheme for DNT:



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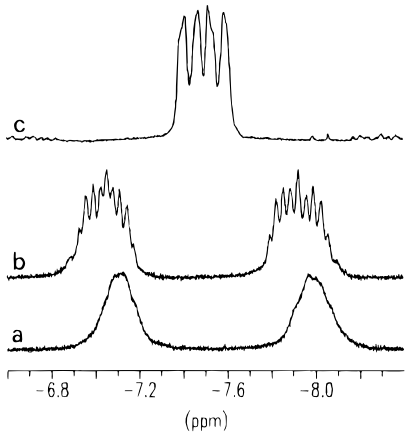

Figure 2. ^{1}H NMR (a, 70 °C; b, 20 °C) and ^{1}H{^{31}P} NMR (c, 20 °C) resonances of the hydride ligands in **7** (THF-d_8, 200.13 MHz).

time scale. Compound **5** is formed quantitatively also by reaction of **4** with $HBF_4 \cdot OEt_2$.[15] The evolution of H_2 during the reaction was seen by ^{1}H NMR spectroscopy (*in situ* experiment).

Reaction of (triphos)Rh(H)$_3$ (6) with DNT in a Sealed NMR Tube. A. NMR Experiment. A 5 mm NMR tube was charged with a THF-d_8 (0.8 mL) solution of **6** (40 mg, 0.06 mmol) and a 3-fold excess of DNT (50 mg, 0.18 mmol) under nitrogen, flame-sealed, and placed in a NMR probe preheated to 70 °C. The ^{31}P{^{1}H} and ^{1}H NMR spectra of this sample, recorded every 30 min, showed the gradual conversion of **6** to a new product, which we assigned as (triphos)Rh(H)$_2$(SC$_{20}$H$_{13}$) (**7**) on the basis of its ^{31}P{^{1}H} NMR AMNX pattern, of a broad doublet of multiplets at ca. −7.5 ppm in the hydride region of the ^{1}H NMR spectrum (Figure 2a), and of related precedents in the literature.[16,17] Complete conversion of **6** to **7** occurred in ca. 3 h; no intermediate species was observed. The probe was then cooled to room temperature and ^{31}P{^{1}H}, ^{1}H (Figure 2b), and broad-band ^{1}H{^{31}P} NMR spectra were acquired (Figure 2c): ^{31}P{^{1}H} NMR AMNX pattern, δ 37.95 ($J(P_AP_M)$ = 24.71 Hz, $J(P_AP_N)$ = 25.06 Hz, $J(P_ARh)$ = 114.44 Hz, P_A), −1.35 ($J(P_MP_N)$ = 22.91 Hz, $J(P_MRh)$ = 80.05 Hz, P_M), −1.54 ($J(P_NRh)$ = 80.35 Hz, P_N), these parameters have been used for the computer simulation of the experimental spectrum; ^{1}H NMR δ −7.5 (doublet of multiplets, $J(HP_{trans})$ = ca. 170 Hz, 2H, Rh−H); broad-band ^{1}H{^{31}P} NMR δ −7.43 ($J(H_AH_B)$ = 4.09 Hz, $J(H_ARh)$ = 13.03 Hz, Rh−H_A), −7.56 ($J(H_BRh)$ = 13.42 Hz, Rh−H_B), these parameters have been used for the computer simulation of the hydride resonances (ABX spin system) in the experimental spectrum. The tube was then opened under a nitrogen atmosphere, and ^{31}P{^{1}H} and ^{1}H NMR spectra were recorded at room temperature every 2 h. Following the elimination of hydrogen, **7** decomposed, although slowly, to unidentified products. Almost complete decomposition was achieved after ca. 24 h.

B. Synthesis of (triphos)Rh(H)$_2$(SC$_{20}$H$_{13}$) (7). A 10 mm NMR tube was charged with a THF-d_8 (2 mL) solution of **6** (80 mg, 0.12 mmol) and a 3-fold excess of DNT (100 mg, 0.36 mmol) under nitrogen, flame-sealed, and placed into an oil bath at 70 °C for 3 h. After the ^{31}P{^{1}H} and ^{1}H NMR spectra of this sample were recorded at room temperature to test the quantitative formation of **7**, the tube was opened under a nitrogen atmosphere. The solution was cannulated into a Schlenk-type flask and concentrated to dryness under vacuum. The ^{31}P{^{1}H} and ^{1}H NMR spectra of the residue showed the presence of **7** and various decomposition products (ca. 30%).

Attempted Catalytic Hydrogenation of DNT by (triphos)Rh(H)$_2$(SC$_{20}$H$_{13}$) (7) in a Sapphire HPNMR Tube. A 10 mm sapphire HPNMR tube was charged with a THF-d_8 (2 mL) solution of **6** (40 mg, 0.06 mmol) and a 20-fold excess of DNT (320 mg, 1.2 mmol) under nitrogen and then placed into an NMR probe, preheated to 70 °C, for 3 h. After the ^{31}P{^{1}H} and ^{1}H NMR spectra were recorded to test the quantitative formation of **7**, the tube was cooled to room temperature and pressurized with hydrogen to 30 atm. The tube was then placed into the NMR probe preheated to 120 °C. The ^{31}P{^{1}H} and ^{1}H NMR spectra of this sample, recorded every 30 min for 3 h, showed the presence of only **7** during the entire experiment. After the tube was cooled to room temperature and depressurized, a 1 μL sample of the solution was withdrawn by a microsyringe and analyzed by GC and GC/MS. No hydrogenation product of DNT was detected.

Reaction of (triphos)Rh(H)$_2$(SC$_{20}$H$_{13}$) (7) with KOBu^t under a Hydrogen Atmosphere in a Sapphire HPNMR Tube. An HPNMR tube containing a THF-d_8 solution (2 mL) of **7**, prepared as described above from the trihydride **6** (40 mg, 0.06 mmol) and a 3-fold excess of DNT (50 mg, 0.18 mmol), was opened under a nitrogen atmosphere. A 6-fold excess of solid KOBu^t was introduced into the tube, which was then closed and pressurized with hydrogen to 5 atm. The ^{31}P{^{1}H} and ^{1}H NMR spectra of this sample, recorded at room temperature after ca. 12 h, showed the presence of only the trihydride **6**. After the tube was depressurized, the contents were transferred into a Schlenk-type flask and acidified with aqueous HCl to ca. pH 5. A sample of the solution, analyzed by GC and GC/MS, showed the presence of DNT and 1,1′-binaphthalene-2-thiol (GC/MS (EIMS, 70 eV; *m/e* (%)): 286 (100) M^+, 285 (60) $M - H^+$, 253 (47) $M - SH^+$, 252 (54) $M - SH_2^+$, 126 (58) $C_{10}H_6^+$) in a ca. 2:1 ratio.

Catalytic Hydrogenation of DNT by [(triphos)Rh(η^2-MeO$_2$CC≡CCO$_2$Me)]PF$_6$ (8) in the Presence of KOBu^t. In a typical experiment, a solution of the π-alkyne complex **8** (14 mg, 0.014 mmol) in THF (30 mL) and 50-fold excesses of both DNT (198 mg, 0.7 mmol) and KOBu^t (78 mg, 0.7 mmol) were placed into the Parr reactor under a nitrogen atmosphere. After the reactor was pressurized with hydrogen to 30 atm at room temperature, the mixture was heated to 160 °C and then immediately stirred (650 rpm). After 16 h, the reactor was cooled to room temperature and slowly depressurized. The contents of the reactor were transferred into a Schlenk-type flask and acidified with aqueous HCl to ca. pH 5. A sample of the solution, analyzed by GC and GC/MS, showed the following compound distribution: DNT (62(1)%), 1,1′-binaphthalene-2-thiol (38(1)%), 1,1′-binaphthalene (traces, <0.2%). Catalytic reactions carried out in the presence of excess elemental Hg (1000:1) to test the homogeneous character of the reactions gave practically identical results in terms of activity and chemoselectivity.[18]

Results

Reaction of (triphos)Ir(H)$_2$(C$_2$H$_5$) (1) with DNT. The reaction of **1** in THF with DNT at temperatures higher than 100 °C gives a diastereomeric mixture of (triphos)IrH(η^2(*C*,*S*)-C$_{20}$H$_{12}$S) (**3a** and **3b**) in a 3:2 ratio, which is invariant with temperature up to 160 °C. Following the insertion into a C−S bond of DNT, iridium becomes a chiral center[19] and thus originates two diastereomers, as DNT is atropisomeric and exhibits C_2 symmetry.[20] Unfortunately, we were unable to either separate the two diastereomers or grow crystals suitable for an X-ray analysis. Accordingly, the structural

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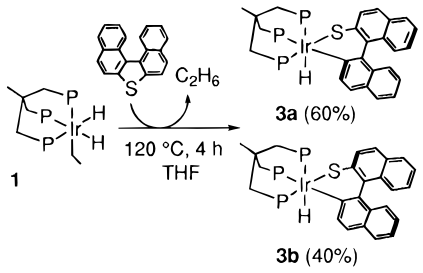
Scheme 2



assignments in Scheme 2 are provisional, in the sense that the labeled stereochemistries for **3a** and **3b** could be the opposite.

The coordination geometry of the stable C−S insertion products **3a** and **3b** can unequivocally be established by multinuclear NMR spectroscopy, as well as by a comparison with the NMR characteristics of the analogous DBT derivative (triphos)IrH(η^2(*C*,*S*)-$C_{12}H_8S$).[7e] In particular, the two diastereomers exhibit temperature-invariant ^{31}P NMR AMQ patterns and distinct ^{1}H and ^{13}C NMR signals for the terminal hydride (*trans* to the most upfield phosphorus resonance) and the metalated carbon atom of the cleaved DNT (J(CP) ≅ 4 Hz).

In situ variable-temperature NMR experiments in THF-d_8 show that the formation of the mixture of **3a** and **3b** is accompanied, even at the early stages of the reaction, by that of another species of the formula (triphos)IrH(η^2-$C_{20}H_{12}S$) (**2**), which persists in solution up to 70 °C and then transforms into the C−S insertion products. Although the exclusive formation of **2** has not been observed at any stage of the reaction between **1** and DNT, the time dependence of the **2**:**3a**,**b** ratio is consistent with a kinetic mixture where the C−S insertion products are thermodynamically more stable than the η^2(*C*,*C*) isomer (Scheme 3).

Compound **2** is obtained in ca. 27% yield by reaction of **1** in THF with DNT at 70 °C for 24 h. Although largely contaminated by the starting complex **1** and by **3a**,**b**, complex **2** can satisfactorily be characterized by ^{31}P{^{1}H} and ^{1}H NMR spectroscopy.

Complex **2** is stereochemically rigid in solution on the NMR time scale. The ^{31}P{^{1}H} NMR spectrum consists of a canonical AMQ pattern, while the ^{1}H NMR contains a resonance at −9.11 ppm (ddd) characteristic of a terminal hydride ligand (J(HP$_{trans}$) = 160.8 Hz, J(HP$_{cis}$) = 14.0, 10.2 Hz). Most importantly, the ^{1}H NMR spectrum also contains a resonance at 5.78 ppm (1H, dd, J(HP) = 8.3 Hz, J(HH) = 7.4 Hz) and a correlated signal at 6.4 ppm (^{1}H,^{1}H 2D-COSY; selective decoupling experiments), which resemble those reported by Jones for the isoelectronic η^2-naphthalene complex (C_5Me_5)-Rh(PMe_3)(η^2-$C_{10}H_8$).[21] The observed multiplicity in the ^{1}H (dd) and broad-band ^{1}H{^{31}P} (d) NMR spectra of the olefin-type hydrogen at 5.78 ppm and the lack of coupling connections between the hydrogen at 6.4 ppm with any other hydrogen nuclei in the molecule suggest that an intact DNT ligand in **2** binds the metal center *via* either the C_6−C_{6a} or C_5−C_6 carbon atoms from a naphthyl ring.[21] Although we cannot exclude either of these bonding modes, we are inclined to favor the η^2(C_6,C_{6a}) coordination for chemical reasons (*i.e.* the lack of C−H activation products during the reaction which transforms **1** into **3a**,**b**; *vide infra*).

When a mixture of **2**, **1**, **3a**, and **3b** in THF-d_8 is pressurized with 3 atm of CO (HPNMR experiment), only **2** reacts with CO at room temperature to give the known hydride carbonyl (triphos)IrH(CO).[14]

The combined chemical and NMR data are thus consistent with a structure for **2** in which iridium is octahedrally coordinated by a *fac* triphos ligand, by a terminal hydride, and by an intact DNT molecule. This uses a naphthyl double bond for coordination. The observation of a single set of NMR resonances for the phosphorus atoms of **2** is consistent with the fact that the iridium atom is not a stereocenter.

Hydrogenation and Protonation of the Iridium C−S Insertion Products. The two diasteromers **3a**,**b** react with H_2 (30 atm) in THF at a temperature higher than 60 °C to give the dihydride thiolate complex (triphos)Ir(H)$_2$($SC_{20}H_{13}$) (**4**) as a racemic mixture (Scheme 4). The result of this reaction parallels that of the analogous DBT derivative (triphos)Ir(H)$_2$($SC_{12}H_9$).[7e,15]

The reaction between the diastereomeric mixture of **3a** and **3b** and H_2 (30 atm) was also studied in an HPNMR tube. No intermediate species was detected during the transformation into **4**. The latter complex is stable in both the solid state and solution.

The elimination of H_2 from **4** is achieved by reaction with a protic acid such as HBF_4·OEt_2 in THF. As was previously observed for the 2-(phenylthio)phenolate dihydride (triphos)Ir(H)$_2$($SC_{12}H_9$),[15] the elimination of dihydrogen (probably *via* direct attack of the added proton at one of the terminal hydrides)[22] is followed by dimerization of the unsaturated fragment [(triphos)IrH-($SC_{20}H_{13}$)] to the stable binuclear complex [(triphos)IrH-(μ-$SC_{20}H_{13}$)$_2$HIr(triphos)](BPh_4)$_2$ (**5**). This dimer is straightforwardly obtained by protonation of **3a**,**b**, a reaction that has been demonstrated to proceed *via* regioselective attack of the proton at the metalated carbon atom.[15]

The lack of mirror symmetry, a consequence of the atropisomeric nature of the 1,1-binaphthalene-2-thiolate ligand, makes all the phosphorus donor atoms (AMQ pattern) and the hydride ligands in the racemic complex **4** chemically and magnetically inequivalent. In contrast, due to the presence of two stereogenic 1,1′-binaphthalene-2-thiolate bridging ligands, two diastereomers (namely the racemate *R*,*R* and *S*,*S* and the *meso* form *R*,*S*) would be expected for **5**. The experimental observation of a single ABM pattern in the ^{31}P{^{1}H} NMR spectrum down to −75 °C suggests that the protonation reactions of **3a**,**b** and **4** proceed with complete diastereoselectivity and afford the more symmetric *meso* form (in the racemate all six phosphorus atoms would be inequivalent). All the other chemicophysical characteristics (NMR, IR, Λ_M, etc.) of **4** and **5** are quite comparable to those of the related BT- and DBT-derived analogs (triphos)Ir(H)$_2$[*o*-S(C_6H_4)C_2H_5], [(triphos)IrH[μ-*o*-S(C_6H_4)C_2H_5]$_2$HIr(triphos)](BPh_4)$_2$,

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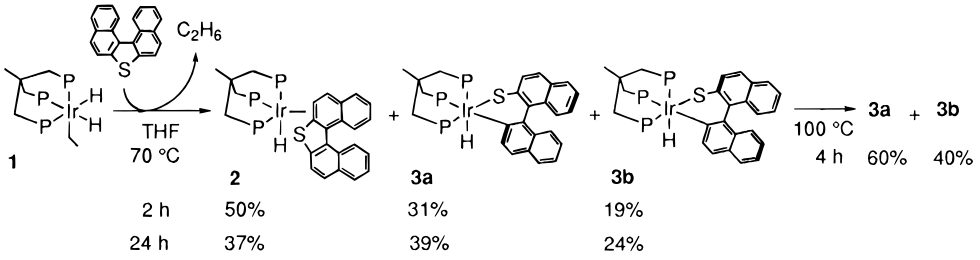
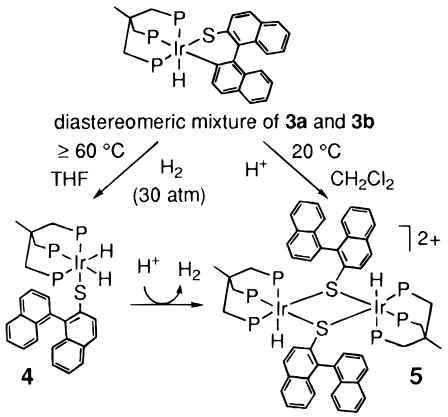
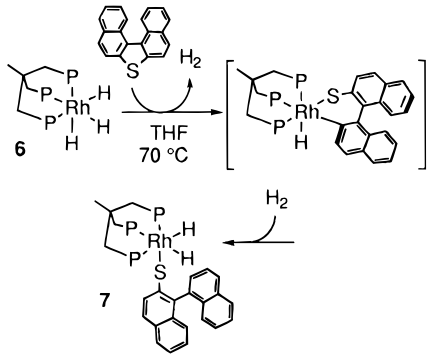
Scheme 3



Scheme 4



Scheme 5



(triphos)Ir(H)$_2$(SC$_{12}$H$_9$), and [(triphos)IrH(μ-SC$_{12}$H$_9$)$_2$-HIr(triphos)](BPh$_4$)$_2$.[7c,e,15] Hence, a detailed description of their spectroscopic properties is not given here.

Reaction of (triphos)RhH$_3$ (6) with DNT. Unlike DBT, whose energy barrier to C−S insertion is too high for the [(triphos)RhH] fragment,[7e,17] DNT is readily cleaved by the 16-electron Rh system even in refluxing THF (Scheme 5). As a result, the dihydride thiolate complex (triphos)Rh(H)$_2$(SC$_{20}$H$_{13}$) (**7**) is quantitatively obtained due to the secondary reaction of the C−S insertion product with H$_2$ generated upon thermolysis of the trihydride precursor **6**.

The hydrogenation of the C−S insertion intermediate is more facile than that of the isolable Ir analogs **3a**,**b** (Scheme 4), consistent with the chemistry of rhodium, which forms weaker metal−carbon bonds than iridium.

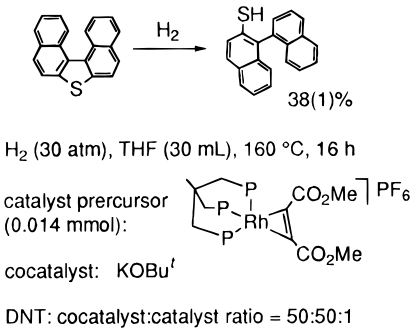
The substitution of Rh for Ir remarkably influences the chemistry of the corresponding (dihydride)thiolate complexes. In fact, under a nitrogen atmosphere, **7** is much less stable than **4** with respect to the loss of H$_2$, an experimental observable that has already been reported for the related 2-(ethylthio)phenolate derivative (triphos)Rh(H)$_2$[*o*-S(C$_6$H$_4$)C$_2$H$_5$].[16] Unlike the latter complex, however, the large size of the 1,1-binaphthalene-2-thiolate ligand prevents the dimerization of the unsaturated fragment [(triphos)Rh(SC$_{20}$H$_{13}$)], which thus decomposes to undefined products.[16,17] Nonetheless, **7** can be isolated in the solid state (although contaminated by some decomposition products, ca. 30%) by rapidly removing the solvent *in vacuo*. Under 30 atm of H$_2$ **7** is stable up to 160 °C.

Due to the lack of mirror symmetry in the molecule, the three phosphorus atoms in **7** are magnetically inequivalent and the ^{31}P{^{1}H} NMR spectrum appears as an AMNX pattern (X = Rh) slightly perturbed by second-order effects. This has successfully been computed with the parameters given in the Experimental Section. The second-order perturbation affecting the equatorial phosphorus nuclei complicates the resonances of the *trans* hydride ligands, which are magnetically inequivalent. As is shown in Figure 2b, the hydride resonances appear at room temperature as a doublet of multiplets (J(HP$_{trans}$) = 170 Hz) which could not be computed. The ^{1}H{^{31}P} NMR spectrum (Figure 2c) is much less complicated and could successfully be simulated as an ABX spin system with the following parameters: δ(H$_A$) −7.43, J(H$_A$H$_B$) = 4.09 Hz, J(H$_A$Rh) = 13.03 Hz; δ(H$_B$) −7.56, J(H$_B$Rh) = 13.42 Hz.

Catalytic Hydrogenolysis of DNT. In earlier work, we have shown that the [(triphos)RhH] fragment is an active catalyst for the homogeneous hydrogenation of BT to 2-(ethylthio)phenol.[16] Under identical conditions (THF, 30 atm of H$_2$, 160 °C), no hydrogenolysis of DNT occurs when **6** is employed as catalyst precursor. A similar result has more recently been observed for the hydrogenolysis of T catalyzed by [(triphos)RhH] and has been attributed to the weak basicity of the sulfur atom of T.[17] The poor ligand capability of T substantially contributes to slow down the rate-determining step (for both BT and T the proposed rate-determining step is the reductive elimination of the thiol from the dihydride thiolate species; *vide infra*).[16,17] In order to increase the reaction rate of T hydrogenolysis, a basic coreagent (KOBu^t, KOH, or NaOMe) was successfully employed.[17] It was suggested that the strong base promotes the elimination of the thiol by formation of a thiolate salt. We have experimentally proved in this work that indeed KOBu^t reacts with the dihydride thiolate complex **7** in the presence of H$_2$ (5 atm) to give the trihydride **6** and potassium 1,1′-binaphthalene-2-thiolate even at room temperature.

The addition of a strong base in a concentration equivalent to that of the thiophene is a winning strategy also for the hydrogenolysis of DNT catalyzed by the [(triphos)RhH] system, as shown in Scheme 6. However, since **6** independently reacts with strong bases to give unreactive species, the π-alkyne complex [(triphos)-Rh(η^2-MeO$_2$CC≡CCO$_2$Me)]PF$_6$[10] (**8**) was employed as catalyst precursor. The latter compound, in fact, is

Scheme 6



capable of generating the [(triphos)RhH] fragment by treatment with H_2 in the presence of strong bases.[17] Accordingly, strong bases have a dual role (cocatalyst and coreagent) in the present hydrogenolysis of DNT, which occurs in the homogeneous phase (mercury test).[18]

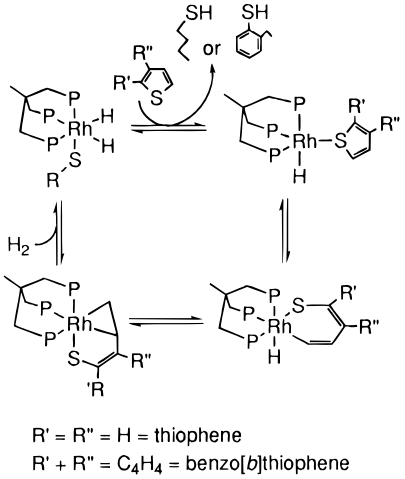
The hydrogenolysis rate of DNT is rather low (19 mol of substrate/mol of catalyst consumed in 16 h), but the catalytic system is quite robust (80% conversion in 48 h).

Discussion

Activation of DNT at the 16-Electron [(triphos)MH] Fragments. Understanding the modes of adsorption of thiophenes at the metal centers on the catalyst surface is of paramount importance for the mechanistic elucidation of the HDS process. In recent years, valuable information in this field has been provided by studies of the modes of coordination of thiophenes in organometallic complexes.[4] Homogeneous modeling studies have also strengthened ties between the bonding mode of the thiophene and its subsequent chemical reactivity: $\eta^1(S)$ thiophenes may be precursors to C−S bond scission[23] (and hence to hydrogenolysis),[4g] while $\eta^2(C,C)$ thiophenes may be intermediates to either C−H bond cleavage or double-bond hydrogenation.[4d,23]

The present study of the interaction of DNT with iridium, which belongs to the class of HDS promoters,[24] shows that this fused-ring thiophene can approach the metal *via* a naphthyl ring ($\eta^2(C,C)$ bonding mode). We do not see, however, the formation of kinetic C−H cleavage products paralleling or preceding the formation of the C−S insertion products **3a**,**b**. This result is surprising, if one recalls that the [(triphos)IrH] fragment reacts with DBT to give C−H and C−S insertion products in parallel paths over the temperature range from 120 to 160 °C.[7e] Above 160 °C, C−S bond cleavage prevails over C−H bond cleavage. Competitive C−H and C−S scissions have been observed also for T and BT activation at [(triphos)IrH][7b] as well as other 16-electron metal systems (*e.g.* $(C_5Me_5)Rh(PMe_3)$).[23] In all cases, it has been concluded that C−H bond cleavage is kinetically competitive with C−S bond cleavage, but the latter is thermodynamically preferred. Since there is no evidence whatsoever for C−H insertion products during the reaction sequence **1** → **2** → **3a**,**b**, one may conclude that, in the peculiar case of DNT, the activation energy for C−S insertion is lower than that of C−H insertion, most likely a consequence of the inherent ring strain in the DNT molecule (the energy barrier to C−S insertion is actually much higher for DBT than for DNT).[8,19] In other words, C−S insertion would be a downhill process after slippage of DNT in **2** from $\eta^2(C,C)$ to $\eta^1(S)$[23,25] (S-bound complexes are, in fact, the immediate precursors to T, BT, and DBT C−S cleavage by low-valent metal complexes).[23] In a sense, the $\eta^2(C_6,C_{6a})$ structure of **2** as given in Scheme 2 fits better than the $\eta^2(C_5,C_6)$ one with a mechanism which involves a low-energy $\eta^2(C,C)$ to $\eta^1(S)$ slippage.

Scheme 7



The enhanced kinetic activity of rhodium *vs* iridium does not allow us to detect any intermediate species during the interaction of the [(triphos)RhH] fragment with DNT, but there is no reason to exclude the possibility that the two 16-electron systems behave similarly. In the case of Rh, the H_2 evolved upon thermolysis of **6** rapidly converts the C−S insertion product to the dihydride thiolate complex **7**.

Rh-Catalyzed Hydrogenolysis of DNT. HPNMR spectroscopy combined with the isolation and characterization of key species related to catalysis has provided a substantial contribution to the understanding of the mechanism of hydrogenolysis of BT and T to 2-(ethylthio)phenol and 1-butanethiol, respectively, catalyzed by [(triphos)RhH] (Scheme 7).[16,17]

Irrespective of the thiophene, the proposed rate-determining step is the elimination of the thiol from the dihydride thiolate intermediates, a process which is influenced by the steric and electronic nature of the substrate. For example, the hydrogenolysis of BT is much faster than that of T, because the latter molecule is a poorer σ-donor ligand and does not efficiently promote the elimination of the corresponding thiol.[16,17,26] In order to increase the hydrogenolysis rate, external reagents capable of trapping the thiol have been successfully employed.[17] As a result, under identical reaction conditions, the rates of hydrogenolysis of both BT and T catalyzed by [(triphos)RhH] have been found to increase remarkably when a strong base such as $KOBu^t$ was added to the catalytic mixtures.[17] The role of the

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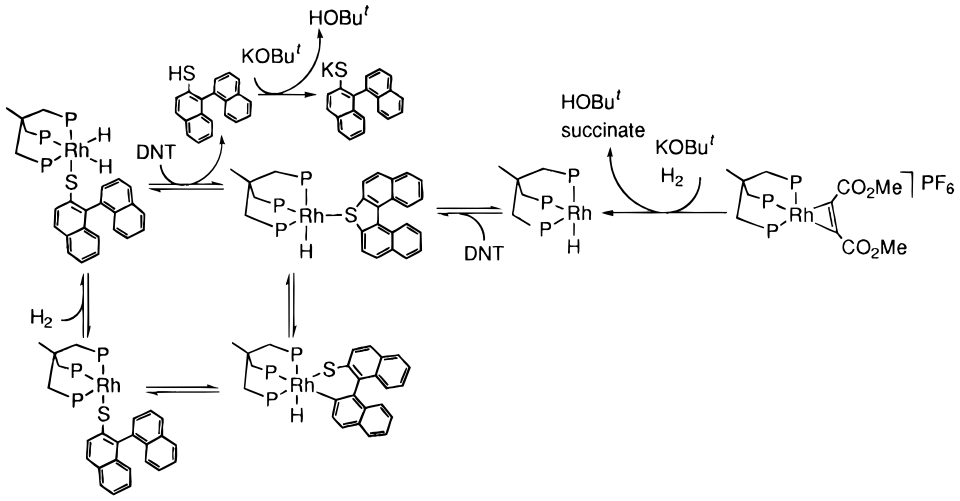
Scheme 8



base is essentially sacrificial when the catalyst is [(triphos)RhH], whereas the base acts also as a cocatalyst when the starting (triphos)Rh complex does not contain hydride ligands (*i.e.* the π-alkyne complex **8**, which generates the [(triphos)RhH] fragment by heterolytic splitting of H_2).[7c,17] Since the base delivers the eliminated thiol into the solution as a thiolate salt, the fastest hydrogenolysis rates are obtained for equivalent concentrations of substrate and base.

The base-assisted reactions cannot be studied by HPNMR spectroscopy for technical reasons (the risk of damaging the sapphire tube is too high). Thus, it cannot be proved experimentally that the hydrogenolysis of DNT catalyzed by [(triphos)RhH] follows the general mechanism reported for T and BT. On the other hand, there is no reason to think of alternative mechanisms if one takes into account all the experimental evidence and chemical arguments discussed here, which ultimately lead to the catalysis cycle proposed in Scheme 8. This begins with the interaction of [(triphos)RhH] with DNT to give an $\eta^1(S)$ adduct which is appropriate to C−S insertion. After C−S bond cleavage, **7** is formed by sequential steps of C−H reductive elimination and H_2 oxidative addition. The 1,1′-binaphthalene-2-thiolate dihydride is a stable complex since, unlike BT,[16] DNT alone is not capable of promoting the elimination of the thiol due to steric effects. At this point, the strong base comes into play: the elimination of the thiol as a thiolate salt occurs, and the catalyst is regenerated.

The slow rate of transformation of DNT (1.2 mol (mol of catalyst)$^{-1}$ h^{-1}) is consistent with the large size of this substrate. Under similar reaction conditions, in fact, BT is hydrogenated to 2-(ethylthio)phenol 40 times faster, despite the less nucleophilic character of its sulfur atom.[7,17,26] On the other hand, the hydrogenolysis of DBT catalyzed by [(triphos)RhH] proceeds with the same rate as for DNT.[17] This result further confirms that the C−S insertion step is not involved in the rate-determining step, as the energy barrier to C−S insertion is lower for DNT than for DBT, while these two substrates contain sulfur atoms of comparable basicity and should exhibit also comparable steric interactions with the metal center.

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