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# Efficient rhodium catalysts for the hydrogenolysis of thiophenic molecules in homogeneous phase

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**Abstract**—In the presence of strong bases, the C—S insertion complexes (triphos)Rh[$\eta^3$-S($C_6H_4$)CH=$CH_2$] and (triphos)Rh($\eta^3$-SCH=CHCH=$CH_2$) as well as the $\pi$-alkyne complex [(triphos)Rh($\eta^2$-$MeO_2CC{\equiv}CCO_2$Me)]$PF_6$ are catalyst precursors for the hydrogenation of thiophene (T), benzo[*b*]thiophene (BT) and dibenzo[*b*,*d*]thiophene (DBT) in tetrahydrofuran solution [triphos = $MeC(CH_2PPh_2)_3$]. Both hydrogenolysis (thiols) and desulfurization (hydrocarbons) products are obtained. Among the substrates investigated, BT is the most reactive, whereas T is the easiest to desulfurize. © 1997 Elsevier Science Ltd

*Keywords*: hydrodesulfurization; catalysis; thiophenes; rhodium; HPNMR spectroscopy.

Hydrodesulfurization (HDS) is the generic name for the heterogeneous catalytic process by which sulfur is removed from petroleum feedstocks upon treatment with $H_2$ [1]. The removal of sulfur compounds (thiophenic molecules, sulfides, disulfides, mercaptans) from fossil fuels is of the upmost importance. From the industrial view, it eliminates the poisoning of catalysts by sulfur during hydrotreating and hydrocracking processes [2]. From the environmental standpoint, it prevents the formation of sulfur oxides when petroleum products are burned.

Commercial HDS catalysts generally comprise supported metal sulfides; Mo or W are essential *components*, but the catalytic activity increases remarkably, particularly towards the thiophenes, by addition of late transition metals (Ni, Co, Ru, Ir, Rh, Pt, Pd, Os, Re) termed *promoters* [3]. The HDS of sulfides, disulfides and mercaptans occurs more efficiently and under milder conditions than that of the thiophenes even on heterogeneous catalysts containing only Mo or W sulfides. Based on this evidence as well as various spectroscopic, theoretical and mechanistic studies, it has been suggested that the active centers for thiophene activation are the promoter atoms, whereas $H_2$ activation occurs on $MoS_2$ or $WS_2$ [1h].

Homogeneous modeling studies [4] support this bifunctional mechanism as the large majority of the known C—S bond scissions of thiophenes [5–11], including hydrogenolysis to thiols [12–15], have been achieved with the use of promoter metal complexes. These, however, are not capable of hydrodesulfurizing the thiophenes unless either Mo (or W) or hydride ligands bound to a second metallic center are contained in the complex framework [16–18]. Three remarkable examples of HDS of thiophenes are illustrated in Scheme 1. A few other examples of stoichiometric desulfurization of thiophenic molecules are known which, however, occur by either thermolysis of polymetallic metal systems containing C—S inserted thiophenes [4h] or reaction of C—S inserted products with external sources of "activated" hydrogen atoms [4h,5a,14].

The proved capability of promoter metal complexes of catalysing the hydrogenolysis of thiophenes to thiols under mild conditions [12b,c] paves the way towards a two-step process to HDS in which pet-

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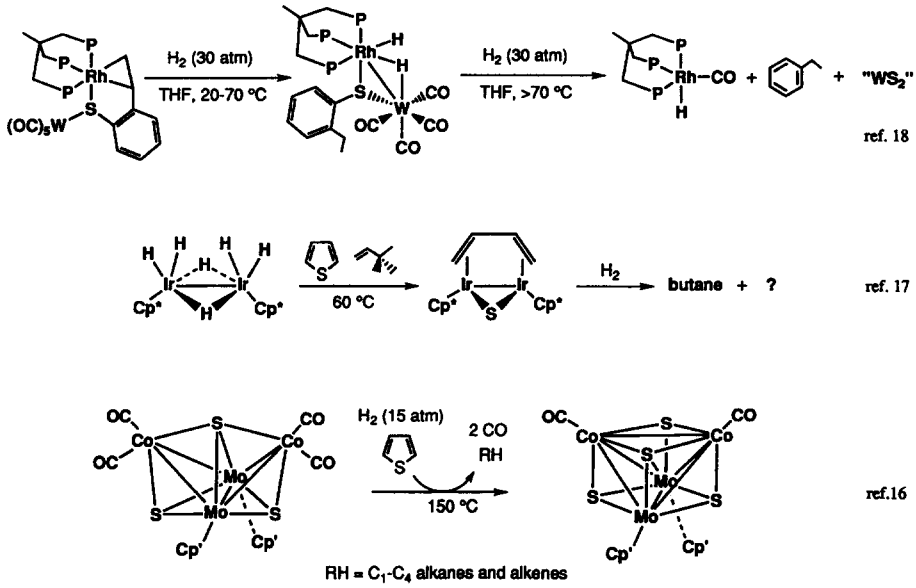
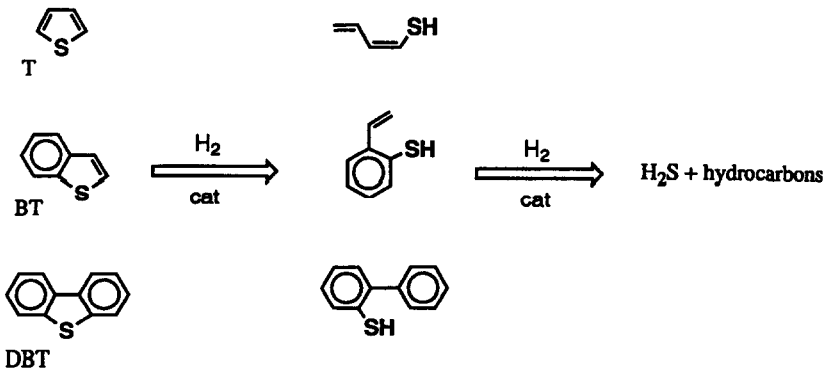



Scheme 1.

roleum is first treated with $H_2$ in the presence of a late transition metal catalyst specifically tailored for the hydrogenolysis of the thiophenes and then hydrogenated in the presence of a conventional HDS catalyst (Scheme 2). This approach involves the development of efficient catalysts for the simple hydrogenolysis of thiophenic molecules to thiols which, in fact, can be desulfurized over conventional catalysts under milder conditions than those required to accomplish the overall HDS of the thiophene precursors. A two-step process of this type would be particularly important for the benzothiophenes and the dibenzothiophenes since the conventional catalysts can desulfurize the corresponding aromatic thiols without affecting the benzene rings, necessary to preserve a high octane rating.

The novelty of this two-step HDS process resides also in the fact that the hydrogenolysis catalysts do not necessarily have to be supported solids. The impressive progress recently achieved in the field of liquid-biphase catalysis [19] opens the door to the application of water-soluble metal complexes also in large-volume industrial reactions such as the hydrotreating of petroleum. In particular, liquid-biphase catalysis could be applied to the purification of distillates from residual sulfur contaminants up to the limit of commercial fuels (where international regulations will soon require reducing the sulfur content to less than 60 ppm) [20].

In our laboratory there has recently been a significant amount of research devoted to finding homogeneous solution-phase Rh catalysts that can perform the hydrogenolysis of benzo[*b*]thiophene (BT) under relatively mild conditions [12c]. The mechanism of these reactions has been elucidated by means of *in situ* spectroscopic methods. This has allowed us to improve the efficiency of the rhodium catalysts with the addition of basic co-reagents, which not only speed up the conversion rate of BT, but also promote both the hydrogenolysis and the desulfurization of otherwise unreactive substrates such as thiophene (T) and dibenzo[*b*,*d*]thiophene (DBT).




Scheme 2.

In the present article we review our work on the Rh-catalysed hydrogenolysis of BT, report our most recent achievements on the catalytic hydrogenolysis of T, BT and DBT, and outline future developments in liquid-biphase HDS catalysis of thiophenes.

## EXPERIMENTAL

### *General information*

All reactions and manipulations were routinely performed under a nitrogen atmosphere by using standard Schlenk techniques. Tetrahydrofuran (THF) was distilled from $LiAlH_4$, stored over molecular sieves and purged with nitrogen prior to use. Thiophene (99+%) was purchased from Aldrich and purified as previously described [5b]. Benzo[*b*]thiophene (99%, Aldrich) and dibenzothiophene (99+%, Aldrich) were sublimed prior to use. Potassium *tert*-butoxide ($KOBu^t$, 95%) and 1-butanethiol (99+%) were purchased from Aldrich and used without further purification. All other chemicals were commercial products and were used as received without further purification. Starting materials [(triphos)Rh($\eta^2$-$MeO_2CC{\equiv}CCO_2Me$)]$PF_6$ [21], (triphos)Rh[$\eta^3$-$S(C_6H_4)CH{=}CH_2$] [5b], (triphos)Rh($\eta^3$-$SCH{=}CHCH{=}CH_2$) [5b] and (triphos)$Rh(H)_3$ [22] were prepared as previously described. Deuterated solvents for NMR measurements were dried over molecular sieves. $^1H$ (200.13 MHz) and $^{31}P\{^1H\}$ (81.01 MHz) NMR spectra were obtained on a Bruker ACP 200 spectrometer. All chemical shifts are reported in ppm ($\delta$) relative to tetramethylsilane, referenced to the chemical shifts of residual solvent resonances ($^1H$) 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 10 mm sapphire high pressure NMR (HPNMR) tube was constructed at I.S.S.E.C.C.-C.N.R. (Firenze, Italy); for the design of the titanum pressure head see [23]. 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 $\mu$m FT) SPB-1 Supelco fused silica capillary column. A 50 m (0.32 mm i.d., 5 $\mu$m FT) CHROMPACK $Al_2O_3$/KCl capillary column was employed for the GC analysis of the gases. GC/MS analyses were performed on a Shimadzu QP 5000 apparatus equipped with a column identical to that used for GC analyses. High-pressure reactions under controlled pressure of hydrogen or carbon monoxide were performed with a stainless steel Parr 4565 reactor equipped with a Parr 4842 temperature and pressure controller.

### *Catalytic runs*

*Catalytic hydrogenation of benzo*[b]*thiophene and dibenzo*[b,d]*thiophene.* The reaction conditions and the results of these experiments have been collected in Tables 1, 2 (BT) and 3 (DBT). In a typical experiment a THF solution of either (triphos)Rh[$\eta^3$-$S(C_6H_4)CH{=}CH_2$] (**2**) or [(triphos)Rh($\eta^2$-$MeO_2CC{\equiv}CCO_2Me$)]$PF_6$ (**7**) in THF together with a 100-fold excess of both the appropriate thiophene and $KOBu^t$ was placed into the Parr reactor under a nitrogen atmosphere. After pressurizing with hydrogen to 30 atm at room temperature, the mixture was heated to 160°C and then immediately stirred (650 rpm). After each run, 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 was withdrawn and analysed by GC and GC/MS. Appreciable production of $H_2S$ (in the form of alkali sulfide) in some catalytic runs was demonstrated by addition of an aqueous $Pb^{II}$ acetate solution under acidic conditions (Laissagne test) to samples of the final reaction mixture. Catalytic reactions were also carried out in the presence of excess elemental Hg (1000 : 1, 1000 rpm) to test the homogeneous character of the reactions. (Note: The reliability of the Hg test to demonstrate the homogeneity of a reaction is not compromised by the presence in the reaction mixture of organic thiols and $H_2S$) [24].

*Catalytic hydrogenation of thiophene.* The reaction conditions and the results of these experiments have been collected in Tables 4 and 5. In a typical experiment a solution of either (triphos)Rh($\eta^3$-$SCH{=}CHCH{=}CH_2$) (**9**) or [(triphos)Rh($\eta^2$-$MeO_2CC{\equiv}CCO_2Me$)]$PF_6$ (**7**) in THF together with a 100-fold excess of both T and $KOBu^t$ was placed into the Parr reactor under a nitrogen atmosphere. A known amount of *n*-octane was also introduced as internal standard for quantitative GC analyses. The reaction mixture was subsequently pressurized with hydrogen to 30 atm at room temperature, heated to 160°C and then immediately stirred (650 rpm). After the time desired, an evacuated gas-collecting loop was connected to the cooled reactor and the gases were collected in the loop placed in an isopentane/liquid nitrogen slush bath. The excess hydrogen was vented and the condensed gases were analysed by GC after being warmed to room temperature. The liquid contents of the reactor were then transferred into a Schlenk-type flask and acidified with aqueous HCl to *ca* pH 5. A sample of the solution was withdrawn and analysed by GC and GC/MS. The production of $H_2S$ was checked out with the Laissagne test. Catalytic reactions were also carried out in the presence of excess elemental Hg (1000 : 1, 1000 rpm) to test the homogeneous character of the reactions.

### *Reactions*

*Reaction of* [(triphos)Rh($\eta^2$-$MeO_2CC{\equiv}CCO_2Me$)]$PF_6$ (**7**) *with hydrogen in the presence of* $KOBu^t$. Solid $KOBu^t$ (0.08 g, 0.7 mmol) was added to a stirred

Table 1. Hydrogenation runs of benzo[*b*]thiophene catalysed by (triphos)Rh[$\eta^3$-S($C_6H_4$)CH=$CH_2$][a]

| Run number | Solvent | $T$(°C) | $PH_2$ (atm) | Time (h) | Reaction composition (%)[b] BT | ETP | DHBT | EB | other | ETP rate[c] |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | acetone | 160 | 30 | 2 | 73(2) | 26(1) | 1(.3) | <0.5 | – | 13.0 |
| 2 | THF | 160 | 30 | 2 | 74(2) | 25(1) | 1(.3) | <0.5 | – | 12.5 |
| 3[d] | THF | 160 | 30 | 2 | 19(1) | 80(1) | 1(.5) | <0.5 | – | 40.0 |
| 4 | acetone | 160 | 30 | 4 | 57(1) | 40(1) | 3(.3) | <0.5 | – | 10.0 |
| 5 | acetone | 160 | 30 | 8 | 52(2) | 45(1) | 3(.3) | <0.5 | – | 5.6 |
| 6 | acetone | 160 | 30 | 12 | 45(1) | 51(1) | 4(.3) | <0.5 | – | 4.2 |
| 7 | acetone | 160 | 30 | 16 | 38(1) | 57(1) | 5(.5) | <0.5 | – | 3.6 |
| 8[e] | acetone | 160 | 30 | 16 | 38(1) | 58(1) | 4(.5) | – | – | 3.6 |
| 9 | THF | 160 | 30 | 16 | 41(1) | 53(1) | 6(.5) | <0.5 | – | 3.3 |
| 10 | acetone | 160 | 15 | 16 | 41(1) | 55(1) | 4(.5) | <0.5 | – | 3.5 |
| 11 | acetone | 160 | 60 | 16 | 35(1) | 60(1) | 5(.3) | <0.5 | – | 3.7 |
| 12 | THF | 120 | 30 | 4 | 97(2) | 2(.5) | 1(.5) | – | – | 0.5 |
| 13 | acetone | 100 | 30 | 16 | 98(1) | 1(.5) | 1(.5) | – | – | <0.1 |
| 14 | acetone | 180 | 30 | 16 | 30(1) | 64(1) | 6(.5) | <0.5 | – | 4.0 |
| 15 | THF | 220 | 30 | 16 | 46(1) | 43(1) | 7(.5) | 4(.5) | <0.5 | 2.7 |
| 16[e] | THF | 220 | 30 | 16 | 51(1) | 43(1) | 6(.5) | – | <0.5 | 2.7 |
| 17[f] | acetone | 160 | 30 | 16 | 34(1) | 61(1) | 5(.5) | <0.5 | – | 1.9 |

[a]Reaction conditions: Parr reactor (650 rpm), catalyst ($4.6 \times 10^{-3}$ M), BT ($4.6 \times 10^{-1}$ M), solvent (30 $cm^3$).
[b]Key: benzo[*b*]thiophene (BT), 2-ethylthiophenol (ETP), dihydrobenzo[*b*]thiophene (DHBT), ethylbenzene (EB).
[c]Rate expressed as mol of ETP (mol of catalyst)$^{-1}$ $h^{-1}$.
[d]Reaction conditions: Parr reactor (650 rpm), catalyst ($4.6 \times 10^{-3}$ M), BT ($4.6 \times 10^{-1}$ M), KOBu$^t$ ($4.6 \times 10^{-1}$ M), solvent (30 $cm^3$).
[e]Reactions carried out in the presence of excess elemental Hg (1000:1; 1000 rpm).
[f]Reaction conditions: Parr reactor (650 rpm), catalyst (4.6 $10^{-3}$ M), BT (2.3 $10^{-1}$ M), solvent (30 $cm^3$).

solution of **7** (0.35 g, 0.35 mmol) in a hydrogen-saturated THF (30 $cm^3$) solution at room temperature. After *ca* 1 h, the solution was equally split into three portions. One portion was maintained under a steady stream of hydrogen at room temperature for a further 1 h. The solvent was then removed *in vacuo* to leave a residue containing the known (triphos)$RhH_3$ [22] (**1**), as the major product (60%), along with some decomposition products ($^{31}P\{^1H\}$ NMR). The second portion, after the hydrogen was replaced by CO, was maintained under a steady stream of CO at room temperature for *ca* 1 h. Removing the volatiles under vacuum gave (triphos)RhH(CO) [22] (**8**, 70%) contaminated by some decomposition products ($^{31}P\{^1H\}$ NMR). The third portion, after the hydrogen was replaced by nitrogen and a two-fold excess of BT (0.03 g, 0.23 mmol) was added, was heated at reflux temperature for 1 h. The reaction mixture was allowed to reach room temperature and then concentrated to dryness under vacuum. The $^{31}P\{^1H\}$ and $^1H$ NMR spectra of the residue showed the presence of (triphos)Rh[$\eta^3$-S($C_6H_4$)CH=$CH_2$] (**2**) only in low yield (*ca* 10%) accompanied by several unidentified rhodium species.

*Reaction of* (triphos)Rh($\eta^3$-SCH=CHCH=$CH_2$) (**9**) *with hydrogen in a HPNMR tube.* A 10 mm sapphire HPNMR tube was charged with a THF-$d_8$ (2 $cm^3$) solution of **9** (0.05 g, 0.061 mmol) under nitrogen, pressurized with hydrogen to 30 atm at room temperature and then introduced into a NMR probe at room temperature. The reaction was followed by variable-temperature $^{31}P\{^1H\}$ and $^1H$ NMR spectroscopy. A selected sequence of $^{31}P\{^1H\}$ NMR spectra is reported in Fig. 1. The reaction between **9** and hydrogen already occurred, even slowly, at room temperature (*ca* 10% in 1 h) yielding a new product characterized as (triphos)$Rh(H)_2(SC_4H_9)$ (**10**) on the basis of its $^{31}P\{^1H\}$ NMR $AM_2X$ spin system {Fig. 1(b), $\delta$ 36.2 [dt, $J(P_ARh)$ = 108.6 Hz, $J(P_AP_M)$ = 24.8 Hz, $P_A$], $\delta$ 0.7 (dd, $J(P_MRh)$ = 80.8 Hz, $P_M$)} and a second-order doublet of multiplets at −7.53 ppm [$J(HP_A)$ = 15.2 Hz, $|J(HP_M)+J(HP_{M'})|$ = 177.4 Hz, $J$(HRh) = 8.4 Hz] in the hydride region of the $^1H$ NMR spectrum. By increasing the temperature to 40°C, the reaction proceeded rapidly [Fig. 1(c)] and **9** almost quantitatively converted to **10** within *ca* 80 min [Fig. 1(d)]. During the conversion of **9** to **10** an intermediate product **11** characterized by a $^{31}P\{^1H\}$ NMR $A_3X$ spin system {$\delta$ 10.5 [d, $J$(PRh) = 130.9 Hz]}, was detected. We tentatively assign this product as (triphos)Rh[$\eta^3$-SCH=CH($C_2H_5$)] (**11**), in which a partially hydrogenated butadienethiolate ligand binds the metal in $\eta^3$-mode (*vide infra*). Raising the temperature to 70°C caused the rapid disappearance of both **10** and **11**. Formed in their place were the known trihydride complex (triphos)$RhH_3$ (**1**) [22] {$^{31}P\{^1H\}$ NMR $A_3X$ spin system, $\delta$ 25.9 [d, $J$(PRh) = 89.6 Hz]; $^1H$ NMR, $\delta$ −7.88 (second-order doublet of multiplets, Rh—H)} and the dimer [($\eta^2$-triphos)Rh($\mu$-$SC_4H_9$)]$_2$ (**12**) (see below) in a 2:1 ratio based on

Table 2. Hydrogenation runs of benzo[*b*]thiophene catalysed by [(triphos)Rh($\eta^2$-$MeO_2CC{\equiv}CCO_2Me$)]$PF_6$[a]

| Run number | Solvent ($cm^3$) | $PH_2$ (atm) | [cat] ($\times 10^3$) | [BT] ($\times 10$) | [KOH] ($\times 10$) | [NaOMe] ($\times 10$) | [KOBu$^t$] ($\times 10$) | Time (h) | Reaction composition (%)[b] BT | ETP | DHBT | EB | ETP rate[c] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | THF (30) | 30 | 4.6 | 4.6 | — | — | — | 2 | 96(2) | 2(.5) | 2(.5) | t | 1.0 |
| 2 | THF (30) | 30 | 4.6 | 4.6 | — | — | — | 16 | 84(2) | 10(2) | 6(1) | t | 0.6 |
| 3 | THF (30) | 30 | 4.6 | 4.6 | — | — | 0.09 | 2 | 75(1) | 24(1) | 1(.3) | t | 12.0 |
| 4 | THF (30) | 30 | 4.6 | 4.6 | — | — | 1.5 | 2 | 70(1) | 28(1) | 1(.3) | 1(.2) | 14.0 |
| 5 | THF (30) | 30 | 4.6 | 4.6 | — | — | 3.1 | 2 | 57(1) | 39(1) | 1(.2) | 3(.4) | 19.5 |
| 6 | THF (30) | 30 | 4.6 | 4.6 | — | — | 4.6 | 2 | 11(1) | 82(2) | t | 7(.5) | 41.0 |
| 7[d] | THF (30) | 30 | 4.6 | 4.6 | — | — | 4.6 | 2 | 18(1) | 76(2) | 1(.3) | 5(.3) | 38.0 |
| 8 | THF (30) | 15 | 4.6 | 4.6 | — | — | 4.6 | 2 | 12(1) | 80(2) | t | 8(.5) | 40.0 |
| 9 | THF (30) | 45 | 4.6 | 4.6 | — | — | 4.6 | 2 | 11(1) | 83(2) | t | 6(.5) | 41.5 |
| 10 | THF (30) | 30 | 4.6 | 4.6 | — | — | 9.2 | 2 | 14(1) | 79(2) | t | 7(.5) | 39.5 |
| 11 | THF (10) | 30 | 4.6 | 18.4 | — | — | 18.4 | 2 | 4(1) | 91(2) | t | 5(.6) | 182.0 |
| 12 | THF (25) MeOH (5) | 30 | 4.6 | 4.6 | — | 4.6 | — | 2 | 20(1) | 79(2) | 1(.5) | t | 39.5 |
| 13 | THF (25) MeOH (5) | 30 | 4.6 | 4.6 | — | 4.6 | — | 16 | 8(1) | 90(2) | 1(.3) | 1(.4) | 5.6 |
| 14 | THF (29) $H_2O$ (1) | 30 | 4.6 | 4.6 | 4.6 | — | — | 2 | 56(1) | 43(1) | 1(.3) | t | 21.5 |
| 15 | THF (29) $H_2O$ (1) | 30 | 4.6 | 4.6 | 4.6 | — | — | 16 | 15(1) | 83(2) | 1(.5) | 1(.3) | 5.2 |
| 16 | THF (29) $H_2O$ (1) | 30 | 4.6 | 4.6 | 0.09 | — | — | 16 | 72(1) | 25(1) | 2(.5) | 1(.4) | 1.6 |

[a]Reaction conditions: Parr reactor (650 rpm); temperature, 160 °C.
[b]Key: benzo[*b*]thiophene (BT), 2-ethylthiophenol (ETP), dihydrobenzo[*b*]thiophene (DHBT), ethylbenzene (EB).
[c]Rate expressed as mol of ETP (mol of catalyst)$^{-1}$ $h^{-1}$.
[d]Reactions carried out in the presence of excess elemental Hg (1000 : 1; 1000 rpm).

Table 3. Hydrogenation runs of dibenzo[*b*,*d*]thiophene catalysed by [(triphos)Rh($\eta^2$-$MeO_2CC{\equiv}CCO_2Me$)]$PF_6$[a]

| Run number | Time (h) | Reaction composition (%)[b] DBT | RSH | RH | RSH rate[c] |
|---|---|---|---|---|---|
| 1 | 2 | 94(2) | 4(2) | 2(.6) | 2.0 |
| 2 | 16 | 77(2) | 19(2) | 4(.5) | 1.2 |
| 3 | 48 | 66(2) | 29(2) | 5(.5) | 0.6 |
| 4[d] | 48 | 67(2) | 29(2) | 4(.5) | 0.6 |

[a]Reaction conditions: Parr reactor, catalyst ($2.3 \times 10^{-3}$M), DBT ($2.3 \times 10^{-1}$M), $KOBu^t$ ($2.3 \times 10^{-1}$M), THF (30 $cm^3$), 160°C, 30 atm of $H_2$.
[b]Key: RSH = 2-phenylthiophenol, RH = biphenyl.
[c]Rate expressed as mol of RSH (mol of catalyst)$^{-1}$ $h^{-1}$.
[d]Reactions carried out in the presence of excess elemental Hg (1000 : 1; 1000 rpm).

Table 4. Hydrogenation runs of thiophene catalysed by (triphos)Rh($\eta^3$-SCH=CHCH=$CH_2$)[a]

| Run number | $T$ (°C) | Time (h) | Reaction composition (%)[b] T | RSH | RH | RSH rate[c] | RH rate[c] |
|---|---|---|---|---|---|---|---|
| 1 | 160 | 2 | 95(2) | 2(1) | 3(1) | 1.0 | 1.5 |
| 2[d] | 160 | 2 | 70(1) | 19(1) | 11(1) | 9.5 | 5.5 |
| 3 | 160 | 16 | 77(1) | 13(1) | 10(1) | 0.8 | 0.6 |
| 4[d] | 160 | 16 | 42(1) | 42(1) | 16(1) | 2.6 | 1.0 |
| 5[d,e] | 160 | 16 | 44(1) | 40(1) | 16(1) | 2.5 | 1.0 |

[a]Reaction conditions: Parr reactor (650 rpm), catalyst ($2.3 \times 10^{-3}$ M), thiophene ($2.3 \times 10^{-1}$ M), THF (30 $cm^3$), 30 atm of $H_2$.
[b]Key: RSH = 1-butanethiol, RH = *n*-butane + butenes.
[c]Rate expressed as mol of RSH (or RH) (mol of catalyst)$^{-1}$ $h^{-1}$.
[d]Reaction conditions: Parr reactor (650 rpm), catalyst ($2.3 \times 10^{-3}$ M), thiophene ($2.3 \times 10^{-1}$ M), $KOBu^t$ ($2.3 \times 10^{-1}$ M), THF (30 $cm^3$), 30 atm of $H_2$.
[e]Reactions carried out in the presence of excess elemental Hg (1000 : 1; 1000 rpm).

Table 5. Hydrogenation runs of thiophene catalysed by [(triphos)Rh($\eta^2$-$MeO_2CC{\equiv}CCO_2Me$)]$PF_6$[a]

| Run number | Time (h) | reaction composition (%)[b] $T$ (°C) | RSH | RH | RSH rate[c] |
|---|---|---|---|---|---|
| 1 | 2 | 84(5) | 8(2) | 8(2) | 4.0 |
| 2 | 16 | 74(3) | 3(1) | 23(2) | 0.2 |
| 3[c] | 16 | 73(3) | 4(1) | 23(2) | 0.2 |

[a]Reaction conditions: Parr reactor (650 rpm), catalyst ($2.3 \times 10^{-3}$ M), thiophene ($2.3 \times 10^{-1}$ M), $KOBu^t$ ($2.3 \times 10^{-1}$ M), THF (30 $cm^3$), 160°C, 30 atm of $H_2$.
[b]Key: RSH = 1-butanethiol, RH = *n*-butane + butenes.
[c]Reactions carried out in the presence of excess elemental Hg (1000 : 1; 1000 rpm).

rhodium {Fig. 1(e) and (f); $^{31}P\{^1H\}$ NMR $AM_2X$ spin system, $\delta$ 27.2 [d, $J(P_MRh)$ = 170.2 Hz, $P_M$], $\delta$ −26.9 (s, $P_A$)}. After this sequence of experiments, the probe was cooled to room temperature, the tube was depressurized to 1 atm $H_2$ and the $^{31}P\{^1H\}$ NMR spectrum was recorded at room temperature [Fig. 2(a)]. The tube was then pressurized with CO to 20 atm and $^{31}P\{^1H\}$ and $^1H$ NMR spectra were recorded after 30 [Fig. 2(b)] and 70 min [Fig. 2(c)]. Compounds **1** and **12** gradually disappeared and formed in their place were (triphos)RhH(CO) [22] (**8**) {$^{31}P\{^1H\}$ NMR $A_3X$ spin system, $\delta$ 17.8 [d, $J$(PRh) = 116.8 Hz]; $^1H$ NMR, $\delta$ −8.04 [qd, $J$(HP) = 34.2 Hz, $J$(HRh) = 13.5 Hz, Rh-H] and (triphos)Rh($SC_4H_9$)(CO) (**13**) {$^{31}P\{^1H\}$ NMR $A_3X$ spin system, $\delta$ 6.2 [d, $J$(PRh) = 104.4 Hz]}, respectively. The $^{31}P\{^1H\}$ NMR data exhibited by **13** agree well with those of the known (*o*-ethylthiophenolate) complex (triphos)Rh(*o*-S($C_6H_4$)$C_2H_5$)(CO) [12c]. In a separate HPNMR experiment the contents of the tube after total conversion of **9**

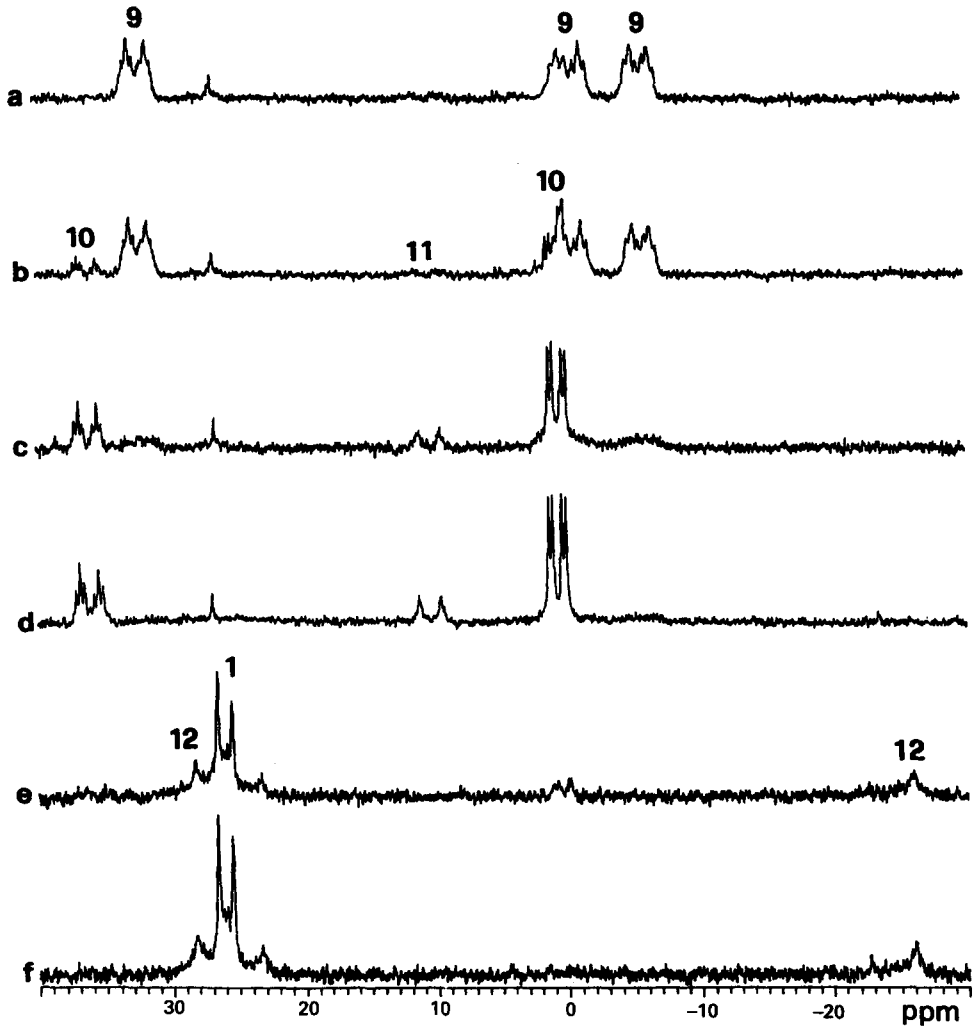



Fig. 1 $^{31}P\{^1H\}$ HPNMR study (sapphire tube, THF-$d_8$, 81.01 MHz) of the reaction of **9** with hydrogen (30 atm $H_2$): (a) at 20°C; (b) after 1 h at 20°C; (c) after 20 min at 40°C; (d) after 80 min at 40°C; (e) after 20 min at 70°C; (f) after 45 min at 70°C.

to **1** and **12,** were analysed by GC-MS showing the formation of 1-butanethiol as the only organosulfur product.

*Synthesis of* (triphos)Rh(H)$_2$(SC$_4$H$_9$) (**10**) *in a HPNMR tube.* A THF-$d_8$ solution (2 cm$^3$) of (triphos)Rh($\eta^3$-SCH=CHCH=CH$_2$) (**9**; 0.05 g, 0.061 mmol) in a 10 mm sapphire HPNMR tube was heated under a hydrogen pressure (30 atm) at 40°C for 2 h. After the probe was cooled to room temperature, the $^{31}P\{^1H\}$ and $^1H$ NMR spectra of this sample recorded at room temperature showed the quantitative formation of **10**. The tube was depressurized to 1 atm $H_2$ and $^{31}P\{^1H\}$ and $^1H$ NMR spectra were recorded every hour at room temperature. Compound **10** quantitatively, although slowly (*ca* 24 h), converted to the dimer [($\eta^2$-triphos)Rh($\mu$-SC$_4$H$_9$)]$_2$ (**12** see below). Pressurization of this solution with hydrogen to 30 atm did not re-form **10** within 24 h.

*Reaction of* (triphos)Rh(H)$_2$(SC$_4$H$_9$) (**10**) *with* CO *in a HPNMR tube.* A solution of **10,** prepared *in situ* as above, was depressurized to 1 atm $H_2$ at room temperature and then pressurized with CO to 20 atm. The $^{31}P\{^1H\}$ and $^1H$ NMR spectra of this sample immediately recorded at room temperature showed the disappearance of **10** and the quantitative formation of (triphos)Rh(SC$_4$H$_9$)(CO) (**13**). The contents of the tube were cannulated into a Shlenk-type and the volatiles were removed under vacuum. In the $^{31}P\{^1H\}$ and $^1H$ NMR spectra of the residue **13** was found to be the only rhodium containing species. $^{31}P\{^1H\}$ NMR (THF-$d_8$, 20°C): $A_3X$ spin system, $\delta$ 6.2 [d, $J$(PRh) = 104.4 Hz]; $^1H$ NMR (THF-$d_8$, 20°C): $\delta$ 2.49 [t, $J$(HH) = 7.4 Hz, 2H, C$H_2$S], *ca* 2 (partially masked by aliphatic protons of triphos, 2H, C$H_2$CH$_2$S), 1.72 (m, C$H_2$CH$_3$, 2H), 1.05 [t, $J$(HH) = 7.4 Hz, 3H, CH$_2$C$H_3$]; IR ($\nu$ CO): 1890 (s) cm$^{-1}$. Compound **13** could also be prepared by reacting THF solutions of the dimer [($\eta^2$-triphos)Rh($\mu$-SC$_4$H$_9$)]$_2$ (**12,** see below) with CO (20 atm) at room temperature in a Parr reactor.

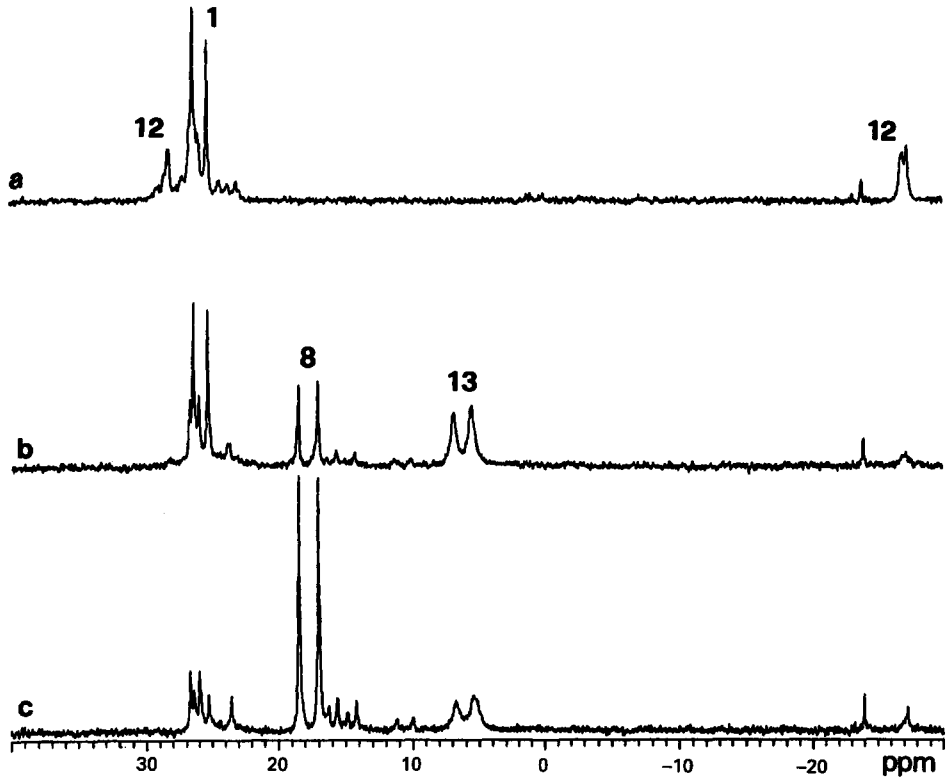



Fig. 2 $^{31}P\{^1H\}$ HPNMR study (sapphire tube, THF-$d_8$, 81.01 MHz) of the carbonylation reaction (20 atm CO, 20°C) of the final mixture obtained by hydrogenation of **9** (trace f of Fig. 2): (a) after depressurization to *ca* 1 atm of $H_2$; (b) after 30 min under CO; (c) after 70 min under CO.

*Preparation of* [($\eta^2$-triphos)Rh($\mu$-$SC_4H_9$)]$_2$ (**12**). A solution of (triphos)$RhH_3$ (**1**; 0.22 g, 0.30 mmol) and 1-butanethiol (0.03 cm$^3$, 0.30 mmol) in THF (50 cm$^3$) was heated at reflux temperature. After 1 h, the reaction mixture was cooled to room temperature and concentrated to *ca* 5 cm$^3$ under vacuum. The portionwise addition of *n*-heptane (30 cm$^3$) led to the precipitation of the dimer **12** as a brown–yellow solid, which was filtered off and washed with *n*-pentane. The compound, extremely air-sensitive in both the solid state and solution even under a nitrogen atmosphere, could not be obtained in analytically pure form. $^{31}P\{^1H\}$ NMR (THF-$d_8$, 20°C): $AM_2X$ spin system, $\delta$ 27.2 [d, $J(P_MRh)$ = 170.2 Hz, $P_M$], $\delta$ − 26.9 (s, $P_A$). $^1H$ NMR (THF-$d_8$, 20°C): $\delta$ 2.51 [t, $J$(HH) = 7.4 Hz, 2H, $CH_2S$], 2.02 (m, $CH_2CH_2S$, 2H), 1.70 (m, $CH_2CH_3$, 2H), 0.98 [t, $J$(HH) = 7.4 Hz, 3H, $CH_2CH_3$].

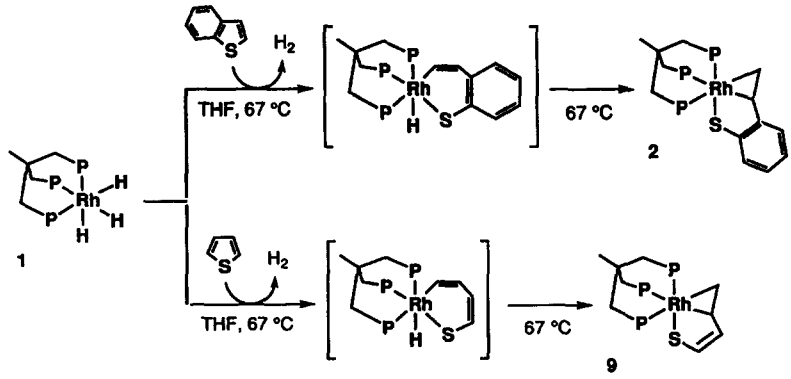
## RESULTS AND DISCUSSION

### *Rh-catalysed hydrogenolysis of benzol*[b]*thiophene*

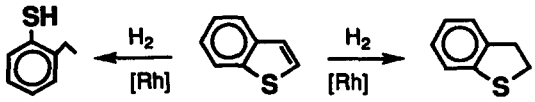
The 16-electron fragment [(triphos)RhH], generated by thermolysis of (triphos)$RhH_3$ (**1**) in refluxing THF, reacts with BT to yield the 2-vinylthiophenolate complex (triphos)Rh[$\eta^3$-$S(C_6H_4)CH{=}CH_2$] [**2**; triphos = $MeC(CH_2PPh_2)_3$] [5b]. The reaction proceeds by regioselective insertion of rhodium into the $C_2$—S bond of BT to give a (hydride) rhodabenzothiabenzene intermediate (Scheme 3). Under the experimental conditions, this latter complex rearranges to **2** by reductive coupling between the terminal hydride and the $\alpha$-carbon of the vinyl moiety of the thiacycle. Experimental evidence for the intermediacy of a hydrido species has been provided by either substitution of Ir for Rh [5f,12a] or reaction of isolated [(triphos)Rh($\eta^2$-*C*,*S*-$C_8H_6S$)]$^+$ with $H^-$ [5e].

Complex **2** is an efficient catalyst precursor for the homogeneous hydrogenolysis of BT to 2-ethylthiophenol (ETP) and, to a lesser extent, for the hydrogenation of BT to dihydrobenzothiophene (DHBT) (Scheme 4) [12c].

Table 1 summarizes selected results obtained in either THF or acetone for different reaction times, temperatures, $H_2$ pressures and substrate concentrations. From a perusal of these data, one may readily infer that the rate of formation of ETP increases with the concentration of BT, whereas it is slightly affected by the $H_2$ pressure (the formation of ETP increases only by 5% in 16 h on going from 15 to 60 atm; runs 10 and 11). Below 15 atm $H_2$, no appreciable hydrogenation of BT occurs even at the highest temperature investigated (180°C) at which the system is still homogeneous. Above this temperature, in fact, the reactions cannot be considered truly homogeneous




Scheme 3.




Scheme 4.

as appreciable production of ethylbenzene (EB) and $H_2S$ occurs in consequence of the formation of Rh metal particles in the reactor (run 15). As a matter of fact, the desulfurization reaction leading to EB is almost totally suppressed when the reactions are performed in the presence of a large excess of elemental mercury (run 16) [24]. A slow but significant production of DHBT, increasing with time (runs 1,2,4–9), is also observed, which has been ascribed to the occurrence of an independent catalysis cycle (*vide infra*).

The catalytic mechanism for the conversion of BT to ETP has been elucidated by high-pressure NMR (HPNMR) spectroscopy combined with the isolation and characterization of key species related to catalysis. A sequence of $^{31}P\{^1H\}$ NMR spectra under catalytic conditions is shown in Fig. 3. When catalytic production of ETP occurs, all rhodium is incorporated into (triphos)$Rh(H)_2[o\text{-}S(C_6H_4)C_2H_5)]$ (**3**) and $[(\eta^2\text{-triphos})Rh\{\mu\text{-}o\text{-}S(C_6H_4)C_2H_5\}]_2$ (**4** trace a). At 100°C, only the dihydride complex **3** is present in the reaction mixture (trace b), whereas after depressurizing and quenching with $N_2$, all rhodium is recovered as the

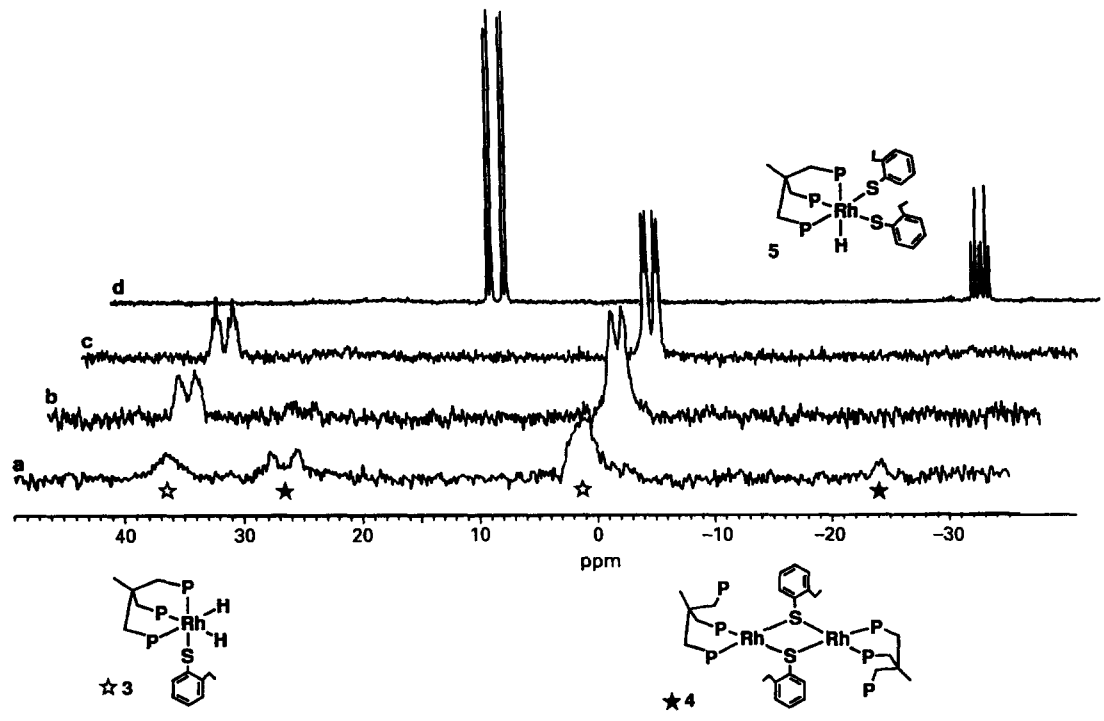
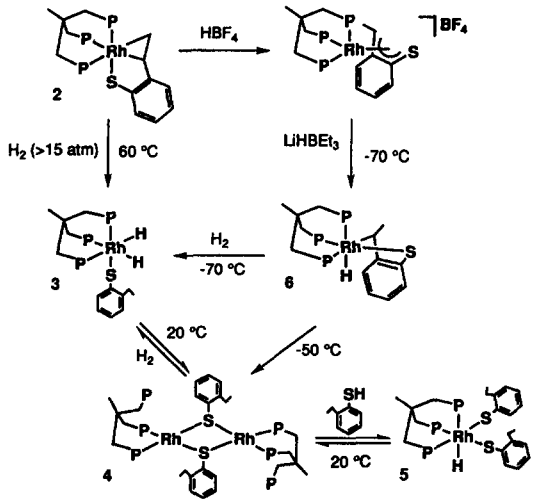



Fig. 3 $^{31}P\{^1H\}$ HPNMR study (sapphire tube, THF-$d_8$, 81.01 MHz) of the catalytic hydrogenation of BT in the presence of **2** (30 atm $H_2$, substrate/catalyst ratio 100): after 4 h at (a) 120°C; after the NMR probe was sequentially cooled to (b) 100 and (c) 80°C; (d) after all hydrogen was replaced by nitrogen (20°C).




Scheme 5.

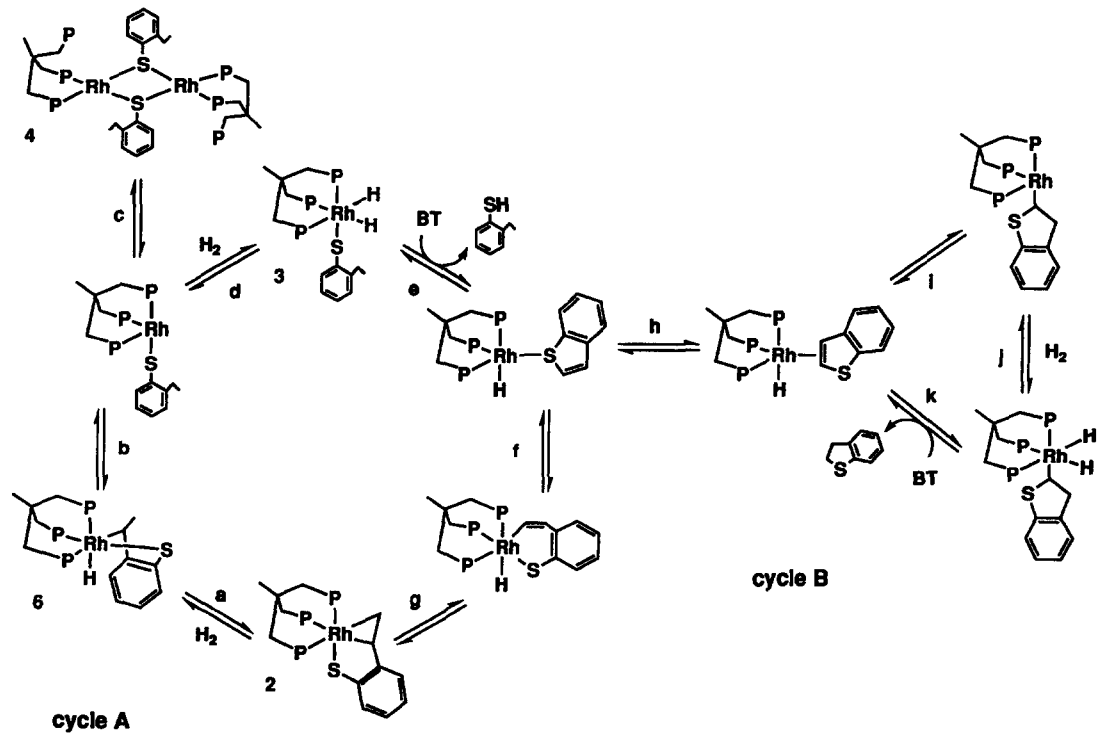
bis-thiolate complex (triphos)RhH[*o*-S($C_6H_4$)$C_2H_5$)]$_2$ (**5**) (trace d), which, in fact, is the terminal metal product of all catalytic runs.

The nature of the chemical transformations that connect compounds **2**, **3**, **4** and **5** has been clarified by a variety of independent reactions with isolated compounds (Scheme 5).

The dihydride complex **3** is quantitatively obtained by reaction of the 2-vinylthiophenolate complex **2** in THF with $H_2$ (>15 atm) at 60°C. Mimicking this reaction (which involves the consumption of two molecules of $H_2$) by the sequential addition to **2** of $H^+$, $H^-$ and $H_2$ shows that the formation of **3** is a stepwise process in which the higher activation energy step is the first $H_2$ uptake to give the (alkyl)hydride (triphos)RhH[$\eta^2$-S($C_6H_4$)CH($CH_3$)] (**6**). The reductive elimination of $H_2$, occurring as a thermal step, transforms **3** into the dimer **4**, which regenerates the dihydride precursor by oxidative addition of $H_2$. Finally, the dimer **4** reacts with ETP yielding the stable bis-thiolate complex **5**.

The catalytic cycle shown in Scheme 6 summarizes all the experimental evidence accumulated for the reaction between BT and $H_2$ catalysed by **2** in the temperature range from 120 to 180°C, where the system is homogeneous.

The cycle (A) begins with the hydrogenation of the 2-vinylthiophenolate ligand in the catalyst precursor to 2-ethylthiophenolate (steps a and b). The resulting fragment [(triphos)Rh{*o*-S($C_6H_4$)$C_2H_5$}] picks up $H_2$ to give the dihydride complex **3** (step d). At the working temperature, **3** can reductively eliminate either $H_2$ or ETP. The reductive elimination of $H_2$ results in the formation of an equilibrium concentration of the dimer **4** (step c), which is inactive towards BT (the slight increase in the catalytic production of ETP at 60 atm has been related to the larger concentration of the dihydride at this pressure). Upon reductive elimination of ETP from **3**, the unsaturated fragment [(triphos)RhH] is formed, which interacts with BT, most likely with formation of an $\eta^1$-*S*-BT adduct (step e). In this bonding mode, BT is activated in such a




Scheme 6.

way that C—S insertion may follow by attack by the electron-rich $Rh^I$ metal on the adjacent carbon atom *via* electron donation into the C—S antibonding orbital [4c,7a,c]. As a result, the (hydride) rhodabenzothiabenzene intermediate **6** is formed (step f), which regenerates the 2-vinylthiophenolate precursor (step g), thus closing the catalysis cycle.

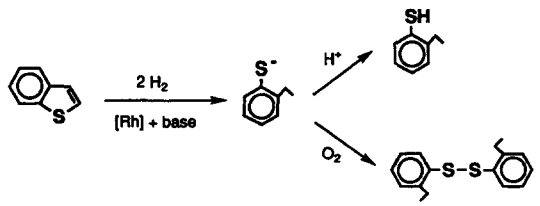
Based on the HPNMR evidence as well as the dependence of the hydrogenolysis rate on both hydrogen pressure and BT concentration, it has been suggested that the reductive elimination of ETP from **3** is the rate-determining step of the catalytic reaction [12c].

As shown in Scheme 6, the observed production of DHBT in all catalytic runs is ascribed to the occurrence of an independent catalysis cycle (**B**) in which the hydrogenation of the $C_2$—$C_3$ double bond of BT occurs through a typical metal-catalysed olefin hydrogenation mechanism, reported also for other examples of Rh-catalysed hydrogenations of BT to DHBT [25,26]. Cycle B requires that the $\eta^1$-*S*-BT intermediate is in equilibrium with an $\eta^2$-2,3-BT isomer, which has precedent in the relevant literature [27]. On the other hand, the [(triphos)RhH] fragment is capable of binding olefins as well as catalysing their hydrogenation [21]. The large prevalence of hydrogenolysis of BT to ETP over hydrogenation to DHBT observed in the present case has been interpreted in terms of the minor steric congestion in the $\eta^1$-*S*-BT adduct compared with the $\eta^2$-2,3-BT isomer [12c,27].

Inspection of Table 1 shows that the best result has been obtained at 180°C and 30 atm run 14). Under these conditions, however, a significant amount of DHBT is also produced (*ca* 6% based on the initial concentration of BT). We have now found that a much better performance of the catalyst precursor **2,** in terms of both activity and chemoselectivity, occurs when a strong base (KOBu$^t$, KOH, NaOMe) in a concentration equivalent to that of BT is added to the catalytic mixture prior to pressurizing with $H_2$. In this case, in fact, the hydrogenolysis rate increases from 12.5 [mol of product (mol of catalyst)$^{-1}$ h$^{-1}$] to 40 (run 3), leading to total consumption of the substrate within 3 h. Moreover, the addition of a strong base improves the chemoselectivity of the reactions as the ETP to DHBT ratio increases remarkably.

At the end of the base-assisted reactions, the hydrogenolysis product is present in the form of potassium (or sodium) thiolate, which can be converted to ETP by acidification with HCl under anaerobic conditions (Scheme 7). Alternatively, the reaction mixture can be exposed to air where the thiolate slowly but quantitatively transforms into the corresponding disulfide [28].

The faster consumption of BT in the presence of a strong base may be explained by taking into account that the reductive elimination of ETP from **3** is most likely the rate-determining step of the catalytic cycle shown in Scheme 6 (step e). This elimination occurs by interaction of **3** with BT, which, however, is a poor



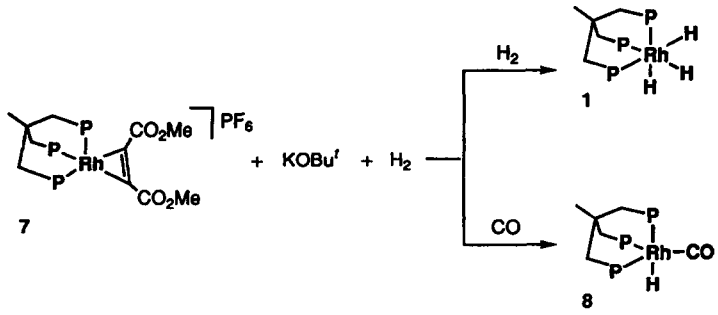

Scheme 7.

ligand and may not promote step e efficiently. The addition of a strong base thus may favor the elimination of ETP, which is delivered into the solution as a thiolate salt. Consistently, it is experimentally observed that the rate of conversion of BT increases with the concentration of the base and reaches a maximum value for a stoichiometric amount of added base (*vide infra*).

In addition to this sacrificial role, strong bases allow one to use other types of catalyst precursors based on the (triphos)Rh moiety, which not necessarily have to contain either C—S inserted thiophenes or terminal hydride ligands. In actuality, any cationic rhodium–olefin complex with triphos may be employed as catalyst precursor. The hydrogenation of such compounds in the presence of strong bases leads, in fact, to the formation of hydrido complexes *via* heterolytic splitting of $H_2$ [29,30]. As a result, the 16-electron [(triphos)RhH] fragment is formed which is the actual catalyst for the hydrogenation of BT assisted by **2**. The π-alkyne complex [(triphos)Rh($\eta^2$-MeO$_2$CC≡CCO$_2$Me)]$PF_6$ (**7**), prepared by mixing (triphos)RhCl($C_2H_4$) with dimethylacetylene dicarboxylate in the presence of $NBu_4PF_6$ [21], is an excellent precursor to the [(triphos)RhH] fragment upon hydrogenation in the presence of KOBu$^t$. As shown in Scheme 8, the [(triphos)RhH] fragment can be trapped by addition of either CO or $H_2$ to give the (carbonyl)hydride complex (triphos)RhH(CO) (**8**) or the trihydride **1,** respectively.

Table 2 summarizes the results of various hydrogenation reactions of BT catalysed by **7** in the presence of strong bases. The role played by the base in the formation of a catalytically active species may readily be inferred from a comparison of runs 1 and 3. In the absence of a base (run 1), **7** is a poor and scarcely selective catalyst precursor. Just the addition of a twofold excess of a strong base (run 3) increases the conversion of the substrate up to the level obtainable by using the 2-vinylthiophenolate precursor **2** (see run 2 of Table 1).

For increasing amounts of added base up to the stoichiometry of the substrate (runs 4–6), the rate of formation of the hydrogenolysis product increases from 14 to 41, while the production of DHBT is almost negligible. From a perusal of Table 2, one may also conclude that: (i) the use of strong bases in larger concentrations than that of the substrate does not practically affect the reaction rate (run 10); (ii) the reaction rates remarkably increase with the con-




Scheme 8.

centration of BT (run 11), whereas they are poorly affected by the $H_2$ pressure in the range 15–45 atm (runs 6,8,9); (iii) a variety of strong bases can be employed (KOBu$^t$, NaOMe, KOH); (iv) the presence of water in the reaction mixture (runs 14–16) slightly decreases the conversion of BT (for which we cannot offer any sound explanation at the moment); (v) the desulfurization of BT to EB increases from 1 to 7% for increasing concentrations of added base (runs 4–6).

A catalytic run carried out in the presence of a large excess of elemental mercury (run 7) does not show a significant variation in both product composition and rate of ETP formation. However, the production of some EB (5%) is still observed. This finding might be related to the formation of a few milligrams of a brown, unsoluble material after each run carried out with the **7**/strong base catalytic system. However, this material, still undefined, neither forms an amalgam with mercury nor catalyses any transformation of BT, as shown by its independent use in a catalytic hydrogenation of the latter substrate. Thus, the formation of some desulfurization product in almost all catalytic runs may also be explained in terms of an independent catalytic cycle assisted by a Rh complex which is formed *in situ*. In other words, the excess of strong base may generate a catalyst that is capable of desulfurizing the thiolate product [3d,16,31]. As a matter of fact, the hydrogenation of **7** in the presence of 2 equiv. of both KOBu$^t$ and BT gives several products among which the 2-vinylthiophenolate complex **2** is only a minor species (any attempt to isolate the other products was unsuccessful due to their extreme instability). On the other hand, the capability of bases to react with metal-activated thiophenes has several precedents in the literature. For example, strong bases may easily abstract a proton from $\eta^1$-*S*-BT or $\eta^1$-*S*-T ligands to give thienyl derivatives [32]. They may also open coordinated thiophenes (particularly in the $\eta^4$-bonding mode) to give butadienethiolate [6a,b], *S*-oxide, hydroxythiophene-yl or acyl thiolate derivatives [10b,d]. Since the use of a large excess of strong bases at high temperature did not allow us to study *in situ* the catalytic reactions by HPNMR due to the risk of damaging the sapphire tubes, any mechanistic rationale for the reactions catalysed by **7** in the presence of bases remains only speculation.

### Rh-*catalysed hydrogenolysis of thiophene*

HPNMR spectroscopy shows that the butadienethiolate complex (triphos)Rh($\eta^3$-SCH=CHCH=$CH_2$) (**9**), prepared by thermolysis of **1** in THF in the presence of T (Scheme 3) [5b], reacts with $H_2$ (30 atm) in a manner which is quite similar to that of the 2-vinylthiophenolate derivative **2**. A sequence of $^{31}P\{^1H\}$ HPNMR spectra is shown in Fig. 1.

The reaction between **9** and $H_2$ already occurs at room temperature (trace b) with the formation, after 1 h, of (triphos)Rh$(H)_2(SC_4H_9)$ (**10**, *ca* 10%) and of traces of another Rh complex (**11**), which is characterized by a $^{31}P$ NMR doublet at 10.5 ppm (see also trace c). Increasing the temperature of the probe-head to 40°C accelerates the transformation of **9** into **10** and **11**, which practically become the only Rh complexes in the reaction mixture after heating at 40°C for further 60 min (trace d). While **10** can readily be authenticated by a comparison of its $^{31}P$ and $^1H$ NMR characteristics with those of the (2-ethylthiophenolate)dihydride **3**, a reliable structural assignment for **11** is complicated by its transient nature as well as its low concentration which precludes a thorough NMR investigation. Tentatively, we assign **11** as the $\eta^3$-1-butenethiolate complex (triphos)Rh[$\eta^3$-SCH=CH$(C_2H_5)$] for the following reasons [13]. Complex **11**, which does not contain hydride ligands, appears contemporaneously with **10** in the NMR spectrum, but disappears more rapidly by further reaction with $H_2$. After 20 min at 70°C, the reaction mixture contains, in fact, **10** (*ca* 10%), the trihydride **1** (*ca* 60%) and the dimer [($\eta^2$-triphos)Rh($\mu$-$SC_4H_9$)]$_2$ (**12**, *ca* 30%, trace e). The latter two compounds and free 1-butanethiol are the only products after 45 min (trace f). Unambiguous authentication of **12** is provided by a comparison of its $^{31}P$ and $^1H$ NMR characteristics with those of the 2-ethylthiophenolate dimer **4** [12c], by its independent preparation by reaction of **1** with 1-butanethiol and by its reaction with CO which gives the (thiolate)carbonyl (triphos)Rh$(SC_4H_9)$(CO) (**13**). As a

further experimental evidence of the final product distribution, the HPNMR tube was depressurized to *ca* 1 atm $H_2$ (Fig. 2, trace a) and then re-pressurized with CO (20 atm). Within 70 min (trace c), both the trihydride **1** and the dimer **12** disappeared. Formed in their place were the known (carbonyl)hydride **8** ($^{31}P\{^1H\}$ NMR doublet at 17.8 ppm) and the (1-butanethiolate)carbonyl complex **13** ($^{31}P\{^1H\}$ NMR doublet at 6.2 ppm, some decomposition products were also formed due to the extreme air-sensitiveness of the dimer).

Both **8** and **13** can independently be synthesized by carbonylation of isolated **1** and **12,** respectively. Unambiguous identification of **13** can be made on the basis of its principal IR and NMR characteristics which are in excellent agreement with those of the previously reported complex (triphos)Rh(CO)[*o*-$S(C_6H_4)C_2H_5$] (similarly prepared by carbonylation of the dimer **4**) [12c]. Compound **13** can also be synthesized by carbonylation of the dihydride complex **10** in THF (20°C, 20 atm of CO). The selective formation of **13** by carbonylation of **10** shows that the reductive elimination of dihydrogen from **10** is favored over thiol elimination [no trace of the (hydride) carbonyl **8** is observed even by HPNMR spectroscopy]. Compound **10** can be generated in solution by hydrogenation of **9** (40°C, 30 atm of $H_2$), but cannot be isolated as it transforms into the dimer **12** in the absence of a positive pressure of $H_2$. Unlike the related dimer **4, 12** does not pick up dihydrogen to give **10** even at room temperature under 30 atm of $H_2$ for 24 h. A diagram summarizing these reactivity studies is presented in Scheme 9.

In light of the chemistry shown in Scheme 9, which is quite similar to that exhibited by the 2-vinylthiophenolate complex **2** (see Scheme 5), one would have predicted for the butadienethiolate complex **9** a role as catalyst precursor for the hydrogenolysis of T at $H_2$ pressures higher than 15 atm and a lower temperature than that required to accomplish the hydrogenolysis of BT by **2**. In actuality, this does not occur unless a strong base is added as a co-reagent (*vide infra*). In fact, as is shown in Table 4, **9** is a very poor catalyst for the transformation of T into mixtures of 1-butanethiol, *n*-butane and butenes (runs 1 and 3). On the other hand, the poor catalytic activity exhibited by **9** is not totally surprising as one considers that its hydrogenation primarily gives the (dihydride)thiolate complex **10,** which is strongly reluctant to eliminate the thiol, whereas it easily loses $H_2$ to form the dimer **12**. This latter complex is a dead-end for the catalytic reaction as is also observed for the hydrogenolysis of BT catalysed by **2** [12c]. Moreover, the much weaker $\sigma$-donor properties of T compared with BT [4] may negatively affect the rate-determining step that, in the BT reaction, has been suggested to be the substrate-assisted elimination of the thiol from the (dihydride)thiolate intermediate (Scheme 6). Just for these reasons, hydrogenation of T to both hydrogenolysis and desulfurization products does need a strong base as co-reagent to occur catalically (Table 4, runs 2 and 4).

From a comparison of runs 4 and 5, one may readily infer that the formation of *n*-butane, largely prevailing over 1- and 2-butenes, is not affected by the presence of a large excess of elemental mercury in the reactor. This evidence and the observation that no decomposition of the catalyst occurs after 16 h are thus consistent with a truly homogeneous hydrogenolysis and hydrodesulfurization catalytic process which has no precedent in the relevant literature for T.

As previously stated, a HPNMR study is not technically feasible. Accordingly, nothing can be said at this stage about the mechanism of the desulfurization step. Given the structural analogy of the catalyst system, it is possible that the HDS step may proceed *via* the mechanism recently proposed for the desulfurization of DBT catalysed by the [(triphos)IrH] fragment [12b]. In this mechanism the C—S cleavage of the metal-bound thiolate was suggested to occur by hydride transfer from the metal to the thiolate C—S carbon atom to give a hydrosulfyl M—SH complex, which eliminates $H_2S$ by action of $H_2$.

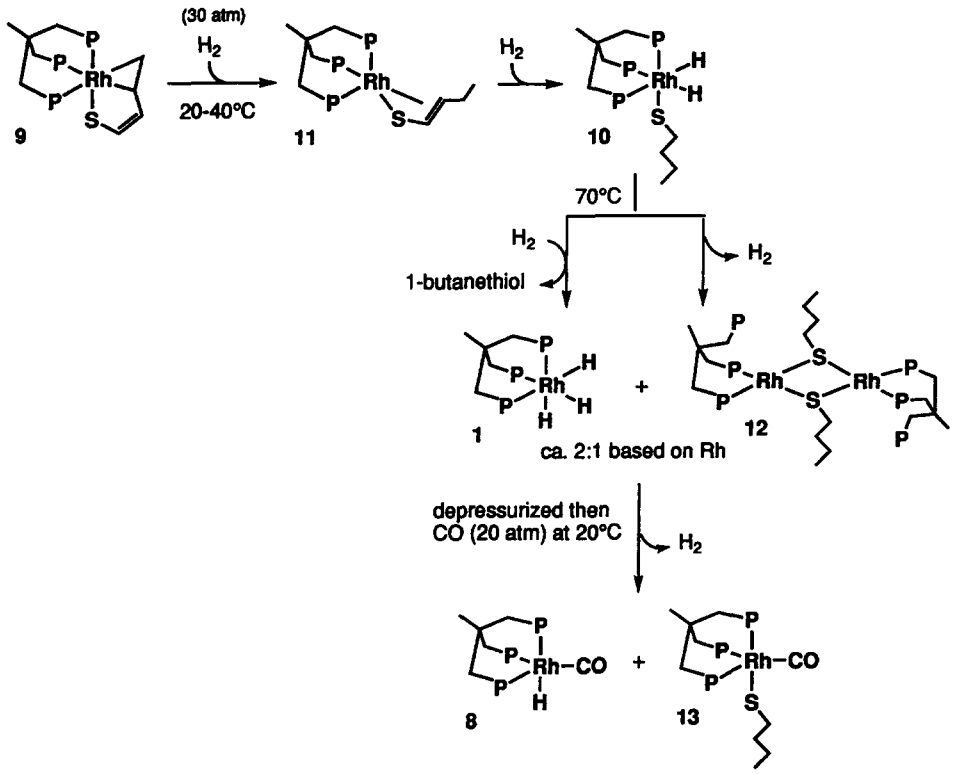
Like BT, the $\pi$-alkyne complex **7** can be employed in conjunction with strong bases as catalyst system for the hydrogenation of T. The results obtained are summarized in Table 5.

The catalytic activity exhibited by the **7**/KOBu$^t$ system is, however, somewhat different from that observed by using **9** as catalyst precursor. In particular, the conversion is much slower (compare run 4 of Table 4 with run 2 of Table 5) and the chemoselectivity changes with prevalence of the desulfurization products. These are formed in almost identical amount even in the presence of elemental mercury (run 3).

The overall catalytic picture is thus quite similar to that observed for the hydrogenation of BT (Table 2), for which we also consider the possibility that the **7**/KOBu$^t$ system may generate under the actual experimental conditions a catalytically active species specifically tailored for the HDS of thiolates.

### Rh-*catalysed hydrogenation of dibenzo*[*b,d*]*thiophene*

DBT is much more refractory to heterogeneous HDS than T or BT [1,3]. Consistently, homogeneous modeling studies agree that DBT opening by metal complexes requires the use of either extremely drastic reaction conditions or highly energetic metal fragments for lowering the energy barrier to insertion. As a matter of fact, unlike the iridium analog [12b], the [(triphos)RhH] fragment is not capable of performing the opening of DBT with the formation of a stable C—S insertion product: the reaction of **1** with DBT invariably results in the extensive decomposition of the (triphos)Rh moiety. For this reason, there is no rhodium C—S insertion product to be used, such as **2** and **9,** as a catalyst precursor for the hydrogenation of DBT. Nevertheless, the catalytic hydrogenation of




Scheme 9.

DBT can be achieved with the 7/KOBu$^t$ system. As shown in Table 3, the rates of conversion of DBT (after acidification) to both 2-phenylthiophenol (hydrogenolysis product) and biphenyl (HDS product) are slightly slower than those observed for T and BT, which is not unexpected in light of the nature of the substrate under investigation.

The formation of appreciable amounts of biphenyl is typical of the catalyst employed and is also practically unaffected by the addition of elemental mercury to the starting reaction mixture (run 4).

## CONCLUSIONS

We have shown in this paper that any kind of thiophenic substrate can be hydrogenated by soluble rhodium catalysts to give either thiols (hydrogenolysis products) or hydrocarbons + $H_2S$ (HDS products). Only in the case of BT appreciable formation of the cyclic thioether (hydrogenation product) may be observed, which is consistent with the more pronunced olefinic character of the $C_2$—$C_3$ bond in BT. The rhodium complexes herein examined as catalyst precursors contain as ancillary ligand the triphosphine triphos. Due to its tripodal geometry, triphos binds metal centers exclusively in a facial arrangement. As a consequence, triphos metal fragments of the type [(triphos)ML] (M = $d^8$ metal ion, L = unidentate ligand) can never attain the stable square-planar structure. For this reason, the [(triphos)RhH] fragment lowers the energy barrier to C—S insertion and promotes under relatively mild conditions the hydrogenolysis of thiophenic molecules, whereas related rhodium or iridium complexes with monodentate phosphine ligands have been found to exclusively hydrogenate thiophenes to the corresponding cyclic thioethers [25,26a,33]. The catalyst precursors employed in this work are either well-defined molecules containing "open" thiophenes or systems prepared *in situ*. In the latter case, a strong base is necessary as a co-catalyst which generates hydride ligands *via* heterolytic splitting of $H_2$. Regardless of the catalyst precursor, we have discovered that strong bases greatly accelerate the reaction rates due to their capability of influencing the rate-determining step (sacrificial role for the elimination of the hydrogenolysis product from the metal center). Other roles may be played by the strong bases, particularly in the catalyst systems generated *in situ*, which, in fact, are much more efficient than the molecular catalysts for the desulfurization to hydrocarbons.

HPNMR studies have shown that in the absence of strong bases, the mechanisms of hydrogenolysis of BT and T are quite similar. For technical reasons the base-assisted reactions have not been investigated by HPNMR spectroscopy. This has precluded a mechanistic interpretation of these reactions, which may involve two independent catalysis cycles (one for the hydrogenolysis, the other for the desulfurization).

The results unequivocally show that T is the sub-

strate which is most prone to desulfurization by soluble metal catalysts, whereas BT is the easiest to degrade, particularly with respect to its hydrogenolysis to 2-phenylthiophenol. The reactivity trend in solution (DBT < T < BT) is in line with the decreasing aromatic character of the thiophenes as well as the trend observed over some heterogeneous HDS catalysts [3c].

Although it is unrealistic to think of using a homogeneous catalyst in a HDS plant, molecular metal complexes may be applied for the purification of distillates in liquid-biphase systems or through their heterogeneization on solid supports. The existing technology for water-soluble phosphine ligands is, in fact, well developed. A water-soluble triphos ligand (sulphos) is also available and has recently been reported to form, in conjunction with rhodium, active liquid-biphase catalysts for the hydrogenation and hydroformylation of olefins [34]. The application of sulphos metal complexes to heterogeneous HDS catalysis is currently under investigation in our laboratory.

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