

Role of single-site catalysts in the hydrogenation of thiophenes: from models systems to effective HDS catalysts

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Abstract

The hydrogenation of thiophenes, leading to cyclic thioethers, thiols or hydrocarbons and H₂S, can be achieved by single-site metal catalysts in both homogeneous and heterogeneous phase. An overview of the processes that have provided useful mechanistic information on hydrodesulfurization catalysis, is presented and commented.

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1. Introduction

Under the push of increasingly stringent environmental regulations concerning the amount of sulfur permitted in gasoline and city diesel, the development of new hydrodesulfurization (HDS) catalysts is a priority in the petrochemical industry [1]. Current HDS technologies are actually capable to reduce the sulfur contents in gasoline and diesel fuel to the marketing limits (<30 ppm in 2006) [2], however this achievement requires a high consumption of energy, with consequent emission of greenhouse gases, and large quantities of hydrogen. Therefore, intense research efforts are being devoted to both improve traditional hydrotreating catalysis and develop alternative strategies for achieving low and ultra low sulfur in fuels.

The sulfur in fossil materials is predominantly contained in thiophenic molecules which comprise a large variety of substituted thiophenes, benzo[*b*]thiophenes, dibenzo[*b,d*]thiophenes as well as other fused-ring thio-

phenes, most of which are generally less easily desulfurized over heterogeneous catalysts than any other sulfur compound in petroleum feedstocks (e.g., thiols, sulfides and disulfides) (Chart 1) [3].

Many new processes have been recently announced to desulfurize and upgrade crude oil, petroleum fractions, fuel and refinery streams. A number of these new technology approaches have become visible which rely on the use of chemical methods to desulfurize diesel and other petroleum streams. Among these are oxidative, using peroxides, peracids, chloramine, persulfates, perboronates [4]; reductive, using water, hydrazine [5]; radiative such as X-ray, ultrasound, photochemistry [6]; enzymatic, using soybean peroxidase and other biocatalysts [7]; aqueous supercritical [5]; *S*-alkylation (sulfonium salt formation) using alkyl halides with promoters [8]; ring alkylations using Friedel–Crafts conditions and agents [9]; selective coordination/adsorption by metal species [10,11]; and carbon–sulfur bond insertion using homogeneous and heterogeneous single-site metal catalysts [12]. The latter approach has not yet led to any practical application, but has provided fundamental mechanistic information on the many elementary steps involved in the primary HDS of fossil fuels.

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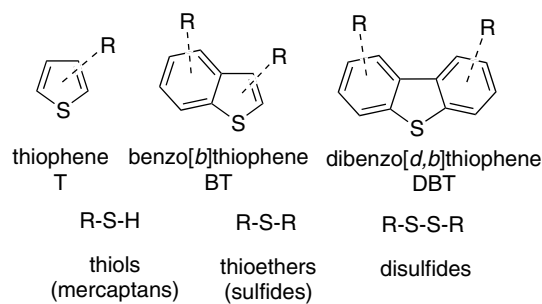


Chart 1.

Indeed, the HDS process (Eq. (1)) in actual refineries occurs by treatment of the feedstocks with a high pressure of H_2 (35–170 bar) at high temperature (300–425 °C) in the presence of heterogeneous catalysts [3].



Commercial catalysts are typically MoS_2 and WS_2 supported on γ -alumina, alone or in conjunction with other late transition metal sulfides (e.g., Co, Ni) that are known as promoters. A detailed understanding of the HDS mechanism, especially as regards the exact location of the metal promoters on the support surface and their function, is still a matter of debate, which hampers a rational design of improved catalytic systems for HDS catalysis.

Large part of the progress made over the last 15 years in the understanding of the HDS mechanism has been provided by studies applying transition metal complexes [12]. From these studies, valuable information has become available on processes whereby thiophenes are coordinated to metal centers, activated so as to undergo either C–H or C–S bond scission, hydrogenated to thioethers, and eventually desulfurized to hydrocarbons. Many of these reactions have been also incorporated into catalytic cycles whose kinetics have been studied in situ under actual catalytic conditions.

This paper presents an overview of the hydrogenation, hydrogenolysis and desulfurization reactions catalyzed by single metal sites in either homogeneous or heterogeneous phase. Most of the reviewed work

involves metal catalysts supported by the tripodal ligand $MeC(CH_2PPh_2)_3$ (triphos) that has been largely developed in our laboratories (Sketch 1) [13].

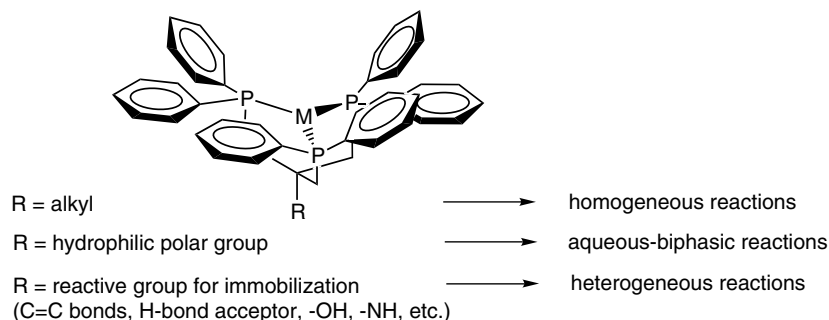
The ligand triphos exhibits several peculiar characteristics that make its metal complexes amenable to use in catalytic reactions under harsh conditions in different phase-variation systems. Indeed, besides forming thermally and chemically stable coordination compounds with almost all transition metals [13], triphos can be easily functionalized so as to allow the immobilization of its metal complexes in either liquid or solid phases. By virtue of this feature, catalysts with identical primary coordination environment can be prepared and used in both homogeneous and heterogeneous processes, providing unique mechanistic information on site-isolation effects.

2. The proposed mechanisms for the HDS of thiophenes

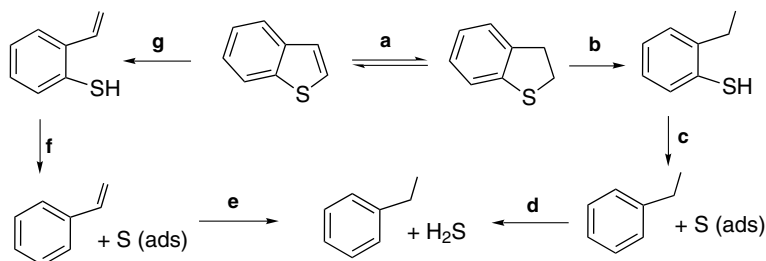
The principal mechanisms proposed for the heterogeneous HDS of a prototypical thiophenic molecule, namely benzo[*b*]thiophene (BT), are illustrated in Scheme 1 [3].

The plain hydrogenation of BT occurs in step a and involves the regioselective reduction of the C_2 – C_3 double bond with formation of 2,3-dihydrobenzothiophene (DHBT). A second hydrogenation involves styrene that is transformed into ethylbenzene in step e. The hydrogenolysis of the C_{sp^2} –S and C_{sp^3} –S bonds occurs in steps g and b, respectively, while the hydrogenolysis of C_{aryl} –S bonds in thiols (desulfurization) closes either cycle (steps f and c).

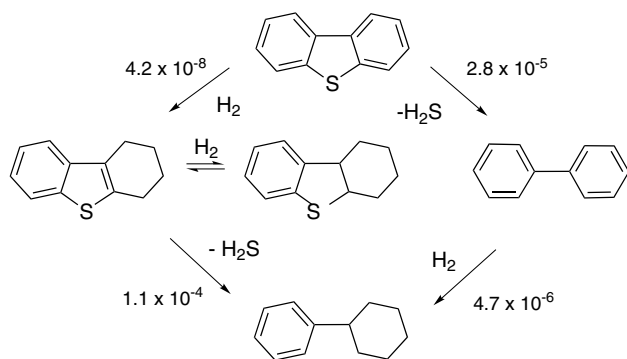
The thiophenes (T) and dibenzothiophenes (DBT) are desulfurized by very similar mechanisms, yet the kinetics of the single steps vary from one substrate to the other [3]. For example, the hydrogenation of DBT to tetrahydrodibenzothiophene or hexahydrodibenzothiophene is more difficult to accomplish than the hydrogenation of T to tetrahydrothiophene (THT) and BT to DHBT and actually represents the rate limiting step in the HDS of DBT (Scheme 2) [3a].



Sketch 1.



Scheme 1.



Scheme 2.

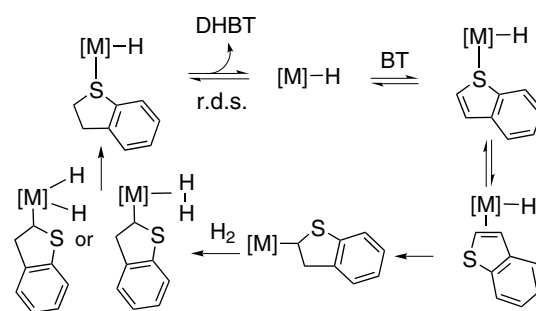
3. Homogeneous hydrogenation reactions

The plain hydrogenation of T and BT to the corresponding cyclic thioether is a process that many homogeneous metal catalysts are able to accomplish under relatively mild experimental conditions [12]. In contrast, no metal complex has been ever reported to promote the hydrogenation of DBT to either tetrahydrodibenzothiophene or hexahydrodibenzothiophene in homogeneous phase, which would be due to the much higher energy barrier to the hydrogenation of aromatic hydrocarbons as compared to *S*-heterocycles.

The hydrogenation mechanism of BT catalyzed by metal complexes comprises steps that are commonly encountered in alkene hydrogenation η^2 -C,C coordination of the substrate (eventually in equilibrium with η^1 -S coordination), addition of H₂ in either oxidative [M(H)₂] or intact form [M(H₂)] (this step may also precede the previous one), hydride transfer to form dihydrobenzothiophenyl, and elimination of DHBT by hydride/dihydrobenzothiophenyl reductive coupling (Scheme 3) [14,15].

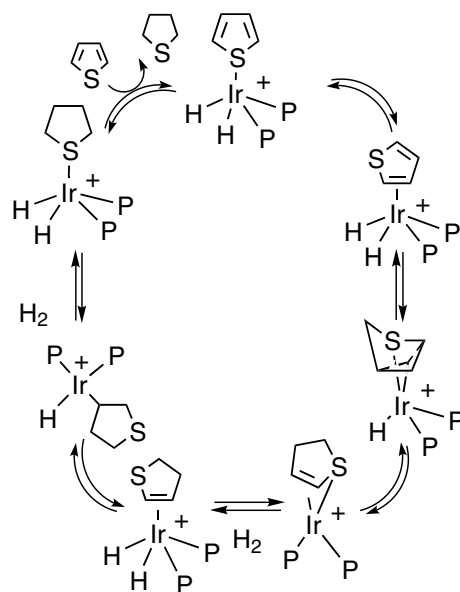
Scheme 3 illustrates the BT hydrogenation mechanism for a model catalyst bearing one hydride ligand as is the case of the 14-e⁻ fragment [(triphos)RuH]⁺ [14].

Overall, the hydrogenation of T is quite similar to that of BT, the only remarkable difference being the regio- and stereospecificity of the first hydride migration step (*endo* migration) to give a thioallyl intermediate. This convert to a 2,3-dihydrothiophene ligand which is



Scheme 3.

then hydrogenated like any other alkene. The substitution of either 2,3- or 2,5-dihydrothiophene for T showed that only the 2,3-isomer was hydrogenated to THT in the presence of the Ir^{III} precursor IrH₂(η^1 -S-T)(PPh₃)₂PF₆ [14a]. Scheme 4 illustrates the hydrogenation mechanism of T as established for the reaction assisted by this Ir catalyst that gave a low conversion due to the formation of a very stable complex between iridium and THT.

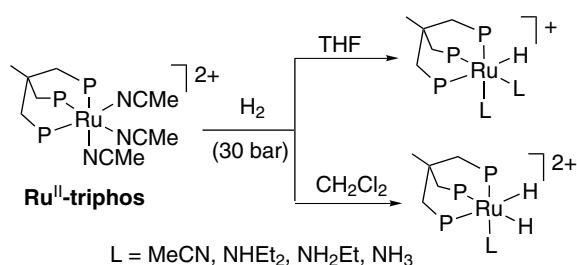


Scheme 4.

Kinetic studies of the hydrogenations of BT to DHBT catalyzed by $[\text{Rh}(\text{PPh}_3)_2(\text{cod})]\text{PF}_6$ [14c] and $[\text{Ir}(\text{PPh}_3)_2(\text{cod})]\text{PF}_6$ [14b] (cod = 1,5-cyclooctadiene) indicated the hydride migration yielding the dihydrobenzothienyl intermediate as the rate-determining step (rds). In contrast, the rds of the reaction catalyzed by $[(\text{triphos})\text{RuH}]^+$ was shown to be the reversible dissociation of DHBT from the metal center [15] (Scheme 3).

Valuable mechanistic information has been obtained by substituting deuterium for hydrogen gas in the reduction of BT to DHBT with the catalyst precursor $[\text{Rh}(\text{MeCN})_3(\text{Cp}^*)](\text{BF}_4)_2$ [16]. The stereoselective *cis*-deuteration of the double bond has been found to be kinetically controlled by the $\eta^2\text{-C, C}$ coordination of BT, while the incorporations of deuterium in the 2- and 3-positions of unreacted substrate and in the 7-position of DHBT have been interpreted in terms of reversible double-bond reduction and arene-ring activation, respectively (Scheme 5).

A number of metal precursors, commonly stabilized by phosphine or cyclopentadienyl ligands, have been reported to generate effective catalysts for the hydrogenation of T and BT, for example: $[\text{Rh}(\text{PPh}_3)_2(\text{cod})]\text{PF}_6$ [17], $[\text{Ir}(\text{PPh}_3)_2(\text{cod})]\text{PF}_6$ [17], $\text{RuCl}_2(\text{PPh}_3)_3$ [17], $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ [17], $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$ [17], $\text{RhCl}(\text{PPh}_3)_3$ [17], $[\text{Rh}(\text{MeCN})_3(\text{Cp}^*)](\text{BF}_4)_2$ [16] and $\text{RuH}_2(\eta^2\text{-H}_2)(\text{PCy}_3)_2$ [18]. As a general trend, the catalytic activity decreases in the metal order $\text{Ru}^{\text{II}} > \text{Rh}^{\text{III}} > \text{Os}^{\text{II}} > \text{Ir}^{\text{III}}$ as well as with increasing nucleophilicity of the solvent that may compete with the thiophene for coordination. The highest activity has been reported for the Ru^{II} catalyst $[(\text{triphos})\text{RuH}]^+$ obtained by hydrogenation of the precursor $[\text{Ru}(\text{MeCN})_3(\text{triphos})](\text{SO}_3\text{CF}_3)_2$ (Ru^{II} -triphos) in nucleophilic solvents, which promote the heterolytic splitting of H_2 [15] (Scheme 6). Instead, in apolar or non-basic solvents, such as CH_2Cl_2 , was formed the 16- e^- system $[(\text{triphos})\text{Ru}(\text{H})_2]^+$, which proved still very active (TOF 1340 vs. 2000 of $[(\text{triphos})\text{RuH}]^+$;



Scheme 6.

TOF = turnover frequency, expressed as mol substrate converted $(\text{mol cat} \times \text{h})^{-1}$ [19].

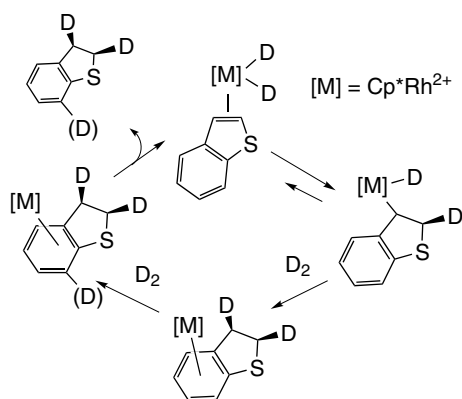
TOFs as high as 2000 were effectively obtained with $[(\text{triphos})\text{RuH}]^+$ in THF (30 bar H_2 , 100 °C). A serious drawback of this system was the deactivation in solvents containing even trace amount of water, due to the formation of the catalytically inactive μ -hydroxo complex $[\text{Ru}_2(\mu\text{-OH})_3(\text{triphos})_2](\text{SO}_3\text{CF}_3)$. In fact, the bases (e.g., amines), which are formed in consequence of the hydrogenation of the MeCN ligands in the precursor (Scheme 6), generate OH^- groups by reaction with adventitious water. Although to a lesser extent, also the catalyst $[(\text{triphos})\text{Ru}(\text{H})_2]^+$ underwent irreversible deactivation at high temperature due to chloride release by the CH_2Cl_2 solvent.

In conclusion, a common feature of all hydrogenation catalysts for T and BT is a modest electron density at the metal center (e.g., d^6 metal ions such as Rh^{III} , Ir^{III} , Ru^{II} or Os^{II}). However, the basicity of the metal center must be finely tuned so as to favour the $\eta^2\text{-C, C}$ coordination of the thiophene over the alternative $\eta^1\text{-S}$ bonding mode, which is precursor to C–S insertion and hence to hydrogenolysis (see below). Conversely, at even nucleophilicity of the metal center, large steric hindrance is generally found to disfavour hydrogenation over hydrogenolysis because the $\eta^2\text{-C, C}$ mode is more sterically demanding than the $\eta^1\text{-S}$ one [15].

4. Aqueous-biphasic hydrogenation reactions with water-soluble catalysts

In aqueous biphasic systems, the hydrogenation reactions of thiophenes (T and BT) to the corresponding cyclic thioether are mechanistically similar to those in truly homogenous phase applying organic solvents. Obviously, the catalyst precursors must be water soluble, which requires the design of ligands bearing polar, hydrophilic groups. The most common of such groups is the sulfonate (SO_3^-) that can be introduced either into *meta* and *para* positions of aryls bonded to phosphorus or into the ligand backbone away from the donor atoms [12].

The use of water-soluble Ru^{II} catalysts to HDS catalysis has been primarily introduced by Sanchez–



Scheme 5.

Delgado and coworkers at INTEVEP S.A. [20]. The precursors $\text{RuHCl}(\text{TPPTS})_2(\text{L}_2)$ (TPPTS = triphenylphosphine trisulfonate; L = amines such as aniline or 1,2,3,4-tetrahydroquinoline) and $\text{RuHCl}(\text{TPPMS})_2(\text{L}_2)$ (TPPMS = triphenylphosphine monosulfonate) were employed to hydrogenate BT in water-decaline under relatively harsh experimental conditions (130–170 °C, 70–110 bar H_2), leading to the selective reduction of the heterocyclic ring. It was observed that nitrogen compounds did not inhibit the hydrogenation of either T or BT, yet in some cases, a promoting effect was observed. These Ru^{II} catalysts were also generated in situ by addition of either TPPTS or TPPMS to water solutions of RuCl_3 .

Later, rhodium and ruthenium catalysts for the selective hydrogenation of BT to DHBT have been obtained with the polydentate ligands ($\text{NaO}_3\text{S}(\text{C}_6\text{H}_4\text{CH}_2)_2\text{C}(\text{CH}_2\text{PPh}_2)_2$ (Na_2DPPPD) [21] and $\text{NaO}_3\text{S}(\text{C}_6\text{H}_4\text{CH}_2\text{C}(\text{CH}_2\text{PPh}_2)_3$ (Nasulphos) (Chart 2), which differ from traditional water-soluble phosphines for the presence of the hydrophilic groups in the ligand backbone, far away from the donor atoms [22]. The Ru^{II} binuclear complex $\text{Na}[\{\text{Ru}(\text{sulphos})\}_2(\mu\text{-Cl})_3]$ [23] and the mononuclear complex $[\text{Ru}(\text{MeCN})_3(\text{sulphos})](\text{SO}_3\text{CF}_3)$ ($\text{Ru}^{\text{II}}\text{-sulphos}$) [15,19,24] showed comparable activity (TOF = 30) in water/decaline or water/*n*-heptane, suggesting the formation of the same catalytically active species, i.e., $[\text{RuH}(\text{sulphos})]$. Like the homogeneous catalyst $[(\text{triphos})\text{RuH}]^+$ in THF, $\text{Ru}^{\text{II}}\text{-sulphos}$ has been reported to undergo deactivation by irreversible transformation into the catalytically inactive μ -hydroxo complex $[\text{Ru}_2(\mu\text{-OH})_3(\text{sulphos})_2]^-$. This degradation pathway was quite fast due to the massive presence of water in the reaction medium.

Some water-soluble catalyst precursors for aqueous-biphasic hydrogenation reactions of thiophenes are illustrated in Chart 2.

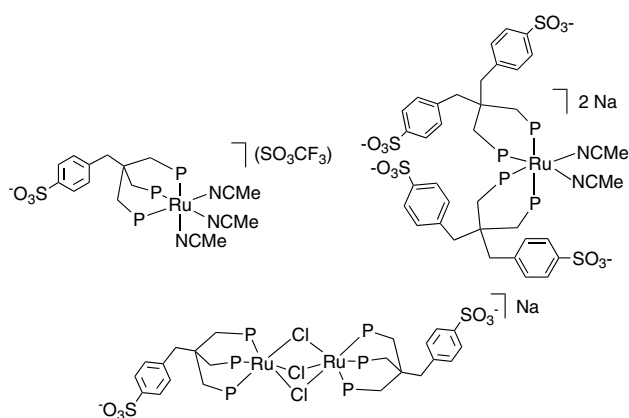


Chart 2.

5. Heterogeneous hydrogenation reactions with immobilized molecular catalysts

Besides using spectator ligands that are not representative of the pools of ligands available to actual HDS catalysts, most homogeneous catalysts are limited by the use of polar solvents that may compete with the sulfur compounds for coordination and reactivity. A further drawback of homogeneous catalysts may be provided by the occurrence of undesired metal–metal interactions via either intermolecular contacts or formation of clusters and aggregates. In order to overcome these limitations and offer more realistic catalytic models, some catalysts of proven efficiency for the hydrogenation of BT and T have been tethered to both organic or inorganic solid supports in such a way to minimize or even eliminate any contact between contiguous metal sites.

The first attempts to hydrogenate sulfur heterocycles with a supported metal catalyst was reported by Fish who immobilized $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ to 2% cross-linked phosphinated polystyrene-divinylbenzene (Chart 3). The tethered catalyst proved able to selectively hydrogenate various heteroaromatics including BT to DHBT (benzene, 85 °C, ≈ 20 bar H_2) with rates three times faster than those observed in homogeneous phase with the parent precursor $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ [25]. This rate enhancement was attributed to steric requirements surrounding the active metal center in the tethered complex, which would favor the coordination of the heterocycles by disfavoring that of PPh_3 .

The most active and fully recyclable single-site catalyst for the hydrogenation of thiophenes in naphthas or model hydrocarbon solvents is still the silica-supported single-site complex $[\text{Ru}(\text{NCMe})_3(\text{sulphos})](\text{OSO}_2\text{CF}_3)/\text{SiO}_2$ ($\text{Ru}^{\text{II}}/\text{SiO}_2$) (Scheme 7). This compound was obtained by tethering the molecular precursor $\text{Ru}^{\text{II}}\text{-sulphos}$ to partially dehydroxylated high-surface area silica through hydrogen-bonds between silanol groups of the support and SO_3^- groups from both the sulphos ligand and the triflate counter-anion [19a]. Upon hydrogenation (30 bar H_2), $\text{Ru}^{\text{II}}/\text{SiO}_2$ generates a very active catalyst for the selective hydrogenation of BT to DHBT with TOFs as high as 2000 (Scheme 7). More importantly, the heterogeneous catalyst $\text{Ru}^{\text{II}}/\text{SiO}_2$ was recycled three times with no significant decay in activity (the TOF was 1960 in the third run). The TOF with $\text{Ru}^{\text{II}}/\text{SiO}_2$ did not practically change even when a new feed containing 2000 equiv of BT in *n*-octane was injected

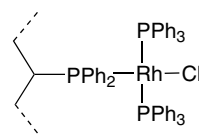
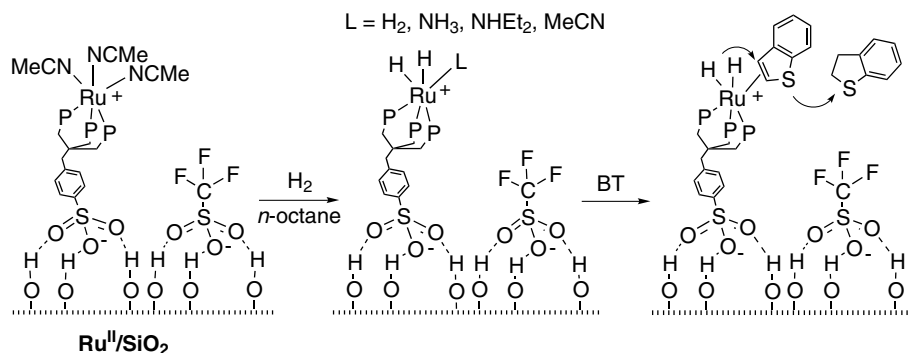


Chart 3.



into the reactor after 1 h reaction, which means that DHBT does not compete with BT for coordination to the Ru^{II} center.

The remarkable stability of Ru^{II}/SiO₂ has allowed its use for the laboratory-scale hydrogenation of real refinery naphthas from Venezuelan crude [26]. As shown in Fig. 1 that reports a GC trace, before and after catalysis, the Ru system is very selective and hydrogenates exclusively the thiophene substrate, leaving intact the other fuel components.

A comparative study of the hydrogenation of various heterocycles, model compounds in raw oil materials, by either Ru^{II}/SiO₂ or Ru⁰ nanoparticles deposited on the same support has been recently reported (Chart 4) [19b]. The nanostructured Ru particles were prepared by calcination/reduction of silica-supported Ru₃(CO)₁₂. Under comparable experimental conditions (30 bar H₂, *n*-octane, 100 °C), Ru⁰/SiO₂ did not catalyze the hydrogenation of BT to any extent, while Ru^{II}/SiO₂ was very active and stable.

It has been proposed that the failure in hydrogenating BT and DBT by Ru⁰/SiO₂ is due to the propensity for adsorption of thiophenes in the unfavourable η¹-S

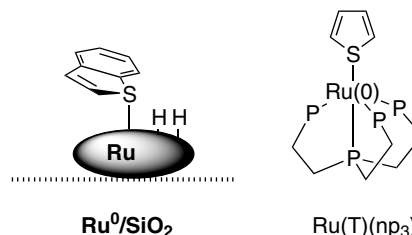


Chart 4.

mode, which does not allow for hydride transfer under the experimental conditions investigated. A similar reactivity has been also observed for the molecular Ru⁰ complex Ru(T)(PP₃) [PP₃ = P(CH₂CH₂PPH₂)₃] that does not undergo hydrogenation of the η¹-S-T ligand (Chart 4) [27]. Other Ru(0) fragments like [RuH(triphos)]⁻ react with BT under H₂ yielding hydrogenolysis products with no appreciable formation of the hydrogenation product DHBT (see below).

Attempts to use combinations of dispersed metal nanoparticles and molecular catalysts covalently tethered on the same support material to promote the hydrogenation of thiophenes have been so far unsuccessful. The technique of combining molecular and nanostructured catalysts on the same support has provided evidence of improved activity in the hydrogenation of arenes and olefins [28] as well as hydrodefluorination of fluoroarenes [29]. An in depth study of the hydrogenation of aromatics by the mixed molecular-nanostructured catalyst Rh(cod)(sulphos)/Pd⁰/SiO₂ (Rh^I-Pd⁰/SiO₂) (Chart 5) showed that the single rhodium sites and the palladium

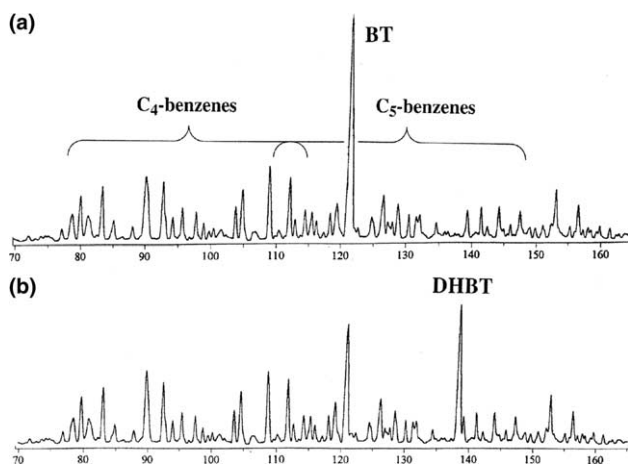
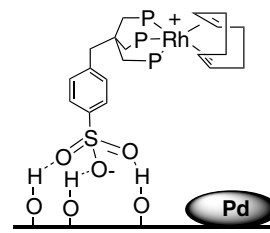
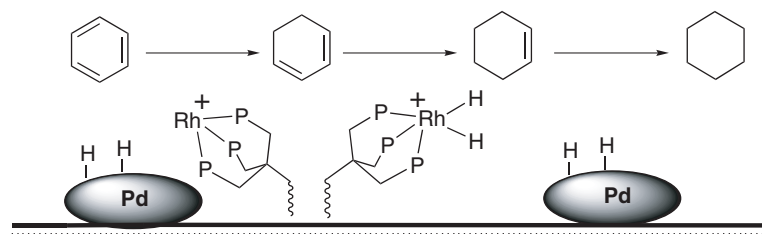


Fig. 1. GC traces of BT-enriched naphtha before (a) and after (b) hydrogenation with Ru^{II}-SiO₂.



Scheme 8. Proposed mechanism for the hydrogenation of benzene by Rh^I-Pd⁰/SiO₂.

particles are in close proximity and may act contemporaneously on the same substrate (Scheme 8) [30].

Rh^I-Pd⁰/SiO₂ has been also tested in the hydrogenation (30 bar H₂) of BT in *n*-octane under 30 bar at 100 °C (Chart 5) [31]. In no case was observed the production of a larger amount of DHBT than that obtained with silica-supported Pd⁰ nanoparticles alone (TOF = 8). Apparently, no synergist effect between the isolated rhodium sites and the surface palladium atoms takes place for the hydrogenation of thiophenes. This was not totally unexpected as neither silica-supported Rh(cod)-(sulphos)/SiO₂ (Rh^I/SiO₂) in *n*-octane [31] nor free Rh(cod)(sulphos) (Rh^I-sulphos) in MeOH or [Rh(cod)(triphos)]PF₆ in THF proved able to hydrogenate appreciably BT and T below 150–170 °C [32]. In fact, at these high temperatures, the hydrogenolysis to the corresponding thiol is known to occur [32b]. Surprisingly, when the hydrogenation of BT in the presence of Rh^I-Pd⁰/SiO₂ was performed at 170 °C under 30 bar H₂ in *n*-octane, only DHBT was produced with a TOF of 20 (corresponding to the activity of the Pd⁰ catalysts at this temperature) with no trace of 2-ethylthiophenol (ETP) [31]. The only explanation that may be offered at this stage is that BT might be preferentially adsorbed by the Pd particles rather than by the close rhodium atom.

6. Homogeneous hydrogenolysis reactions

The reaction which transforms a thiophenic substrate into the corresponding thiol is referred to as hydrogenolysis (Scheme 9).

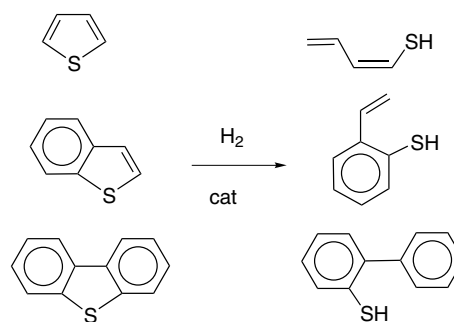
Highly energetic metal fragments with filled orbitals of appropriate symmetry are necessary to lower the barrier to C–S insertion which occurs via *d* π (metal) → π*(C–S) transfer [12,33]. Moreover, the steric crowding at the metal center must be large enough to disfavor the η²-C,C bonding mode of the substrate, but not so large to impede the coordination of the substrate via the sulfur atom. A number of metal fragments have been found to fulfill these requirements, yet only a few, exclusively containing triphos and triphos-derived ligands, have proved able to perform the homogeneous hydrogenolysis of thiophenes in catalytic fashion [32b]. This

because the experimental conditions for hydrogenolysis are relatively harsh (≥160 °C, ≥30 bar H₂) and a strong base is often necessary for high conversions (see below).

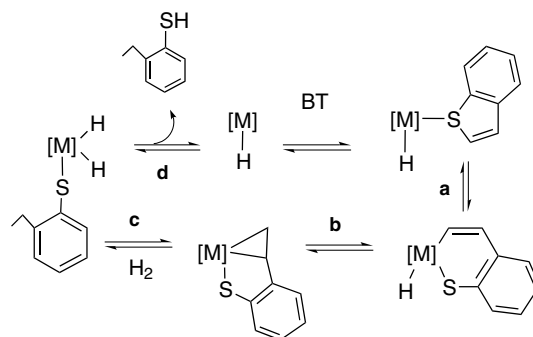
All thiophenes (T, BT and DBT) undergo hydrogenolysis by molecular catalysis through the same mechanism, exemplified in Scheme 10 for BT and a catalyst bearing a hydride ligand [12].

The most efficient hydrogenolysis catalysts, [RhH(triphos)] [32] and [RuH(triphos)]K [24], contain a hydride ligand and a 16-e⁻ electron count. The catalysis cycle involves common steps of C–S insertion (a), hydride migration (b), H₂ oxidative addition (c) and reductive elimination (d).

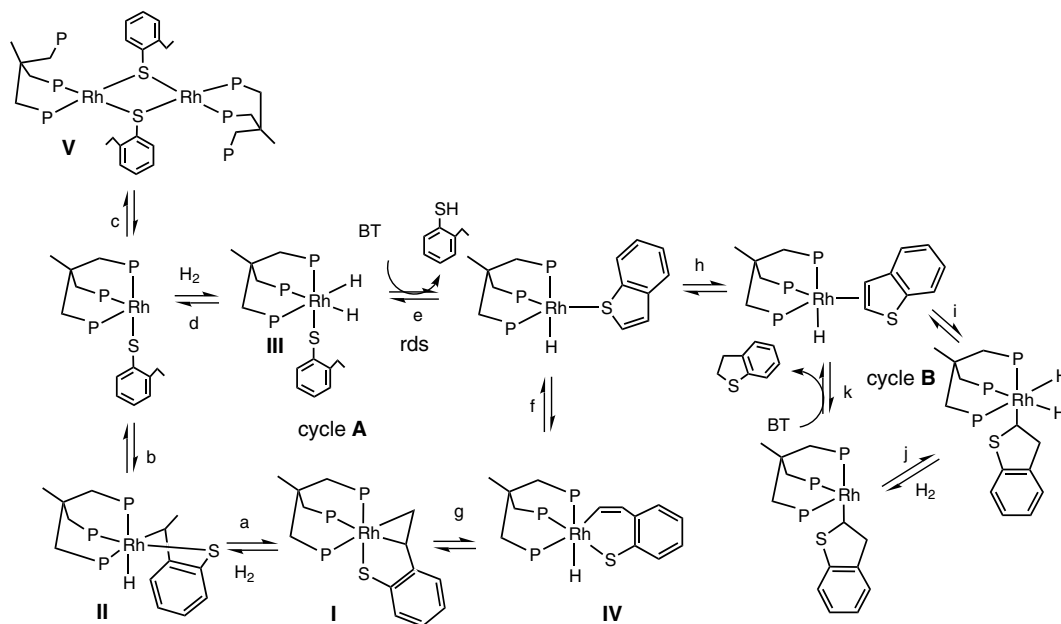
The first catalyst for the homogeneous hydrogenolysis of BT was discovered in 1995 and the detailed mechanism shown in Scheme 11 was elucidated by an in situ high-pressure NMR (HPNMR) study [32c].



Scheme 9.



Scheme 10.



Scheme 11.

The 2-vinylthiophenolate complex $\text{Rh}[\eta^3\text{-S}(\text{C}_6\text{H}_4)\text{-CH}=\text{CH}_2](\text{triphos})$ (I), obtained by thermolysis of the trihydride $\text{RhH}_3(\text{triphos})$ in the presence of BT [34], was actually used as catalyst precursor, yet the trihydride itself or other species capable of generating the 16- e^- fragment $[\text{RhH}(\text{triphos})]$, can equally start the catalysis cycle A. Other intermediates or resting states such as the Rh^{III} hydride II, the dihydride thiolate III, the hydride thiometallacycle IV and the binuclear resting state V were either seen during the catalysis (III and V) or independently synthesized [32c]. Besides ETP, a small amount of DHBT was also produced in consequence to the concomitant occurrence of the hydrogenation cycle B.

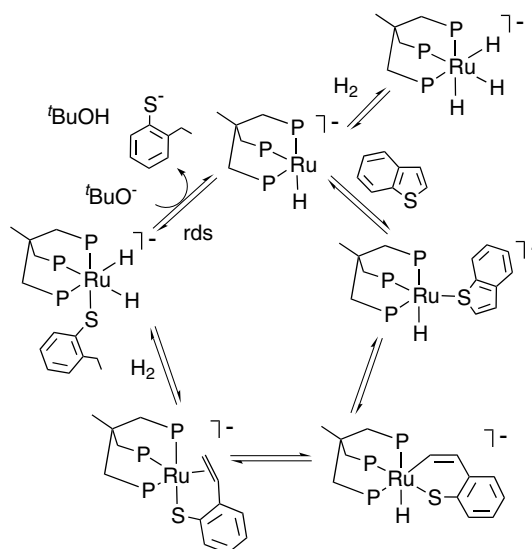
Soon after the discovery of the effectiveness of $[\text{RhH}(\text{triphos})]$ as hydrogenolysis catalyst, it was apparent that the reductive elimination of ETP was the rate-limiting step. Therefore the reactions in THF or acetone were carried out in the presence of a strong base, for example NaOH or KOBU^t , which accelerated remarkably the process, increasing the TOF by about an order of magnitude, and also improving the selectivity [32b]. Best conversions were generally achieved with base concentrations as high as those of the substrate. Kinetic studies have shown that the hydrogenolysis rate is linearly proportional to the concentration of catalyst, substrate and base [32b].

Besides BT, other thiophenes such T [32c], DBT [32c] and dinaphto[2,1-*b*:1',2'-*d*]thiophene [35] have been successfully converted to the corresponding thiolates by $[\text{RhH}(\text{triphos})]$ in the presence of a strong base.

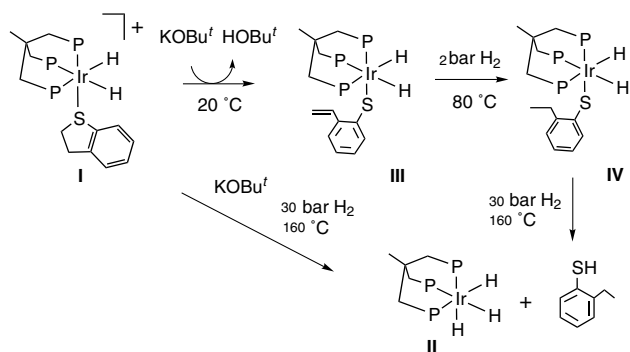
Comparable activity to the rhodium catalysts in the hydrogenolysis of BT has been reported for the Ru^0 system $[\text{RuH}(\text{triphos})]^-$ that is actually isoelectronic

and isostructural with $[\text{RhH}(\text{triphos})]$ [32c]. The hydride Ru^0 catalyst was either isolated or generated in situ by thermolysis of the ruthenate $[\text{RuH}_3(\text{triphos})]\text{K}$ or by hydrogenation in THF of several Ru^{II} precursors in the presence of a strong base, commonly KOBU^t [24]. Mechanistically, the hydrogenolysis of BT with the Ru^0 catalyst is identical to that assisted by the Rh^{I} analogue (Scheme 12).

As shown in Scheme 1, the hydrogenolysis of thiophenes may also proceed via paths a–b, i.e., the hydrogenation precedes the hydrogenolysis of the thioether. Only one example of homogeneous hydrogenolysis of



Scheme 12.



Scheme 13.

thiophenes proceeding via cyclic thioether has been reported so far (Scheme 13) [36].

Under 30 bar H₂ and 160 °C in THF, the DHBT ligand in **I** underwent ring-opening by KOBu^t (E₂ elimination mechanism) yielding the trihydride **II** and free ETP. Independent experiments proved that the ring opening actually occurs at 20 °C and that the rate-limiting step of the overall reaction is the removal of the thiolate ligand from the dihydride **IV**, which is consistent with previous catalytic studies [32].

7. Aqueous-biphasic hydrogenolysis reactions with water-soluble catalysts

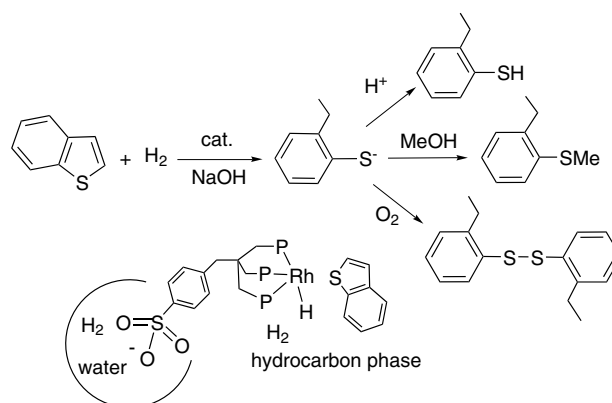
The biphasic hydrogenolysis of BT has been accomplished in water-MeOH-*n*-heptane and water-*n*-decane mixtures with the precursor Rh^I-sulphos that generates the 16-e⁻ catalyst [RhH(sulphos)]⁻ by reaction with H₂ in the presence of a strong base [32a]. Rather harsh reaction conditions (160 °C, 30 bar H₂) and an equivalent amount of NaOH were required for high conversions of BT to 2-ethylthiophenolate. In these conditions, the thiolate product accumulated in the aqueous phase leaving the hydrocarbon phase formally “desulfurized” (Scheme 14). After phase-separation, the thiolate was recovered as thiol, thioether or disulfide.

In situ HPNMR experiments and a kinetic study showed that the aqueous-biphasic hydrogenolysis proceeds with the mechanism established in homogeneous phase (Schemes 11 and 12).

Aqueous-biphasic hydrogenolysis is considered as a very promising polishing procedure for desulfurizing hydrotreated diesel down to low-ppm levels suitable for impending low sulfur fuel regulations. As shown in Fig. 2, the hydrogenolysis of BT with Rh^I-sulphos can be efficiently performed also on real refinery naphtha [37].

8. Heterogeneous hydrogenolysis reactions with molecular catalysts tethered to solid supports

Scheme 15 shows the procedure developed for anchoring the triphosphine moiety –C(CH₂PPh₂)₃ to a



Scheme 14.

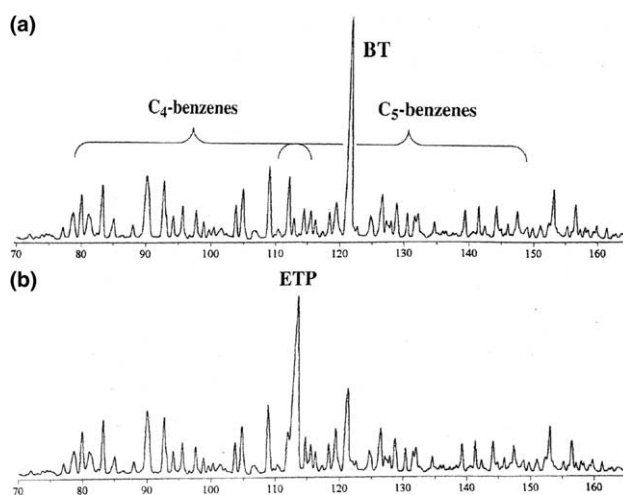


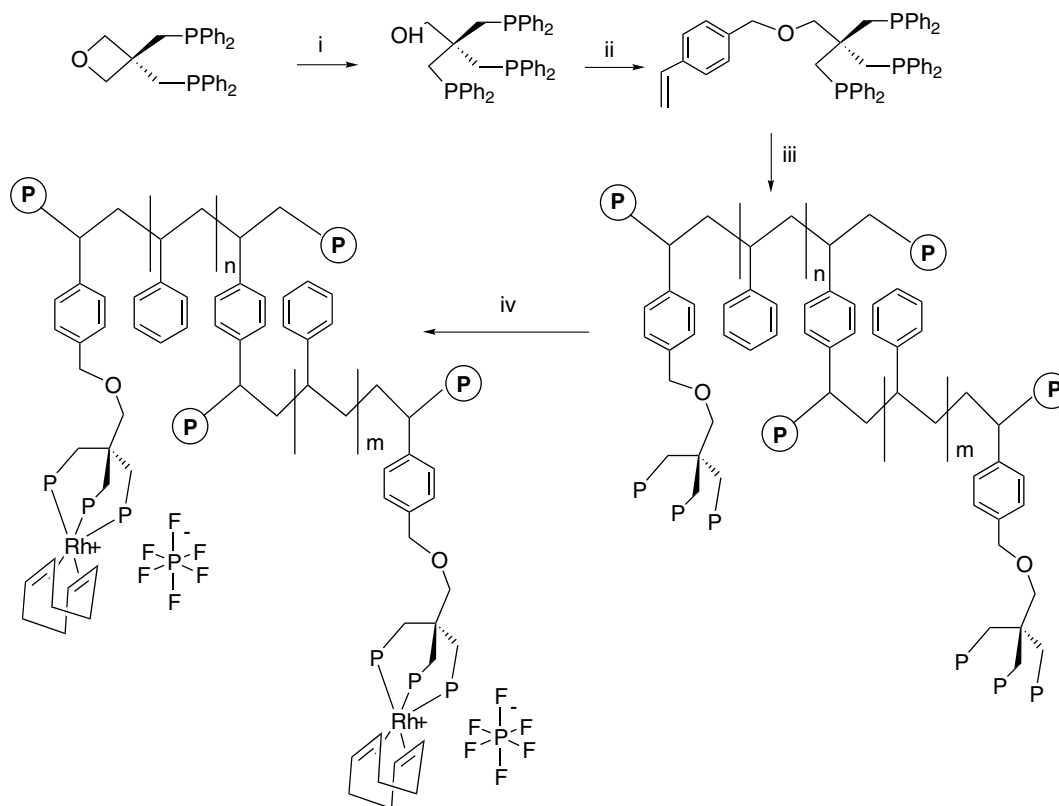
Fig. 2. GC traces of BT-enriched naphtha before (a) and after (b) aqueous-biphasic hydrogenation with Rh^I-sulphos.

cross-linked styrene/divinylbenzene polymer, yielding polymeric triphos (polytriphos) [38]. The reaction of polytriphos with [RhCl(cod)]₂ in CH₂Cl₂ in the presence of AgPF₆ gave the polystyrene-supported complex [Rh(cod)(polytriphos)]PF₆ (Rh^I-polystyrene) with Rh content of ≈1 wt%.

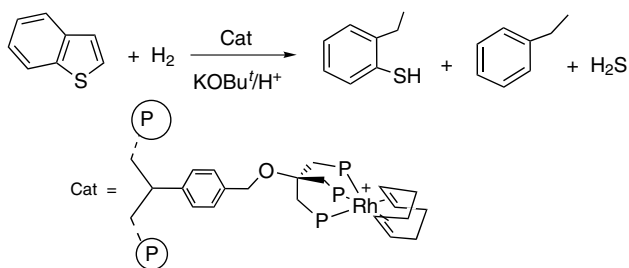
Rh^I-polystyrene is an effective catalyst for the hydrogenolysis of BT to ETP (TOF 48) and ethylbenzene (TOF 2) under rather harsh experimental conditions (THF, KOBu^t, 160 °C, 30 bar H₂) (Scheme 16). No trace of the hydrogenation product DHBT was observed. As well, no rhodium leaching was observed, while the catalyst was recycled several times with no loss of catalytic activity.

The desulfurization of BT to ethyl benzene has been proved to be a truly catalytic process related to the single site catalyst and not to decomposition to Rh⁰ metal (see below).

The heterogeneous hydrogenolysis of BT has been also attempted with other immobilized catalysts such as the silica-tethered precursors Rh^I/SiO₂ and Ru^{II}/SiO₂ [31]. In either case, the H-bond immobilization of



Scheme 15. Reagents and conditions: (i) HPPH₂, BuLi, THF (65%); (ii) NaH, 4-vinylbenzyl chloride, DMF (90%); (iii) styrene-divinylbenzene, AIBN, THF/MeOH (1:2, v:v), 85 °C (80%); (iv) [RhCl(cod)]₂, [Bu₄N]PF₆, CH₂Cl₂ (98%).



Scheme 16.

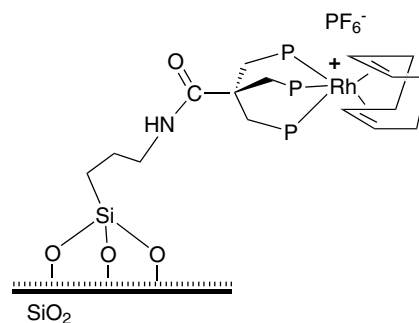


Chart 6.

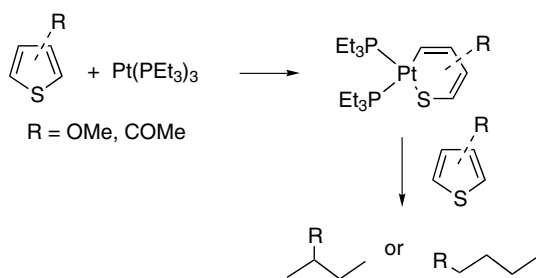
the metal complexes did not tolerate the use of strong bases that are mandatory co-reagents for high activity. Better results have been obtained with the moiety –C(CH₂ PPh₂)₃ covalently tethered to silica as shown in Chart 6 [39]. With this complex, the hydrogenation of BT in THF gave ETP with TOF of 90 (30 bar H₂, KO-Bu^t, 160 °C), yet just after the second cycle, the TOF decreased to 50 due to metal leaching [39].

9. Homogeneous hydrodesulfurization reactions

The homogeneous HDS of thiophenes is a difficult process to accomplish catalytically, and, since it generally requires harsh reactions conditions, the occurrence of

heterogeneous processes promoted by metal particles has been never discarded [3,12b].

The best catalysts reported so far are the thiaplatinacycles shown in Scheme 17, obtained by C–S insertion of Pt(PEt₃)₃ into various substituted thiophenes [40]. The thiaplatinacycle precursors have been reported to desulfurize the thiophenes in either THF or toluene under relatively mild conditions (100 °C, 20 bar H₂) with TOFs from 30 to 80. The highest TOFs were obtained in the presence of elemental mercury that would have the role of incorporating an insoluble “sulfur-containing species” [40a]. Similar dibenzothiaplatinacycles have been reported to undergo stoichiometric desulfurization, the



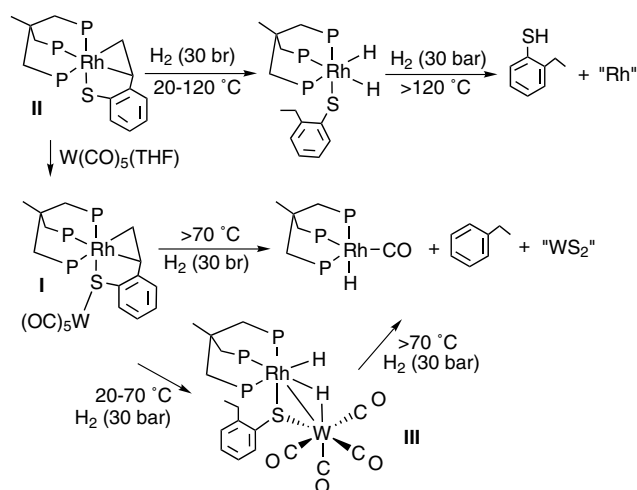
Scheme 17.

amount of which depends on the supporting ligands (phosphine and/or phosphite) as well as the use of alumina in the reaction media [40b].

Evidence for the formation of hydrocarbons has been also observed in a number of reactions of T, BT and DBT catalyzed by Rh and Ir triphos precursors under hydrogenolysis conditions [32b,38,41]. In most cases, however, the reactions were conducted under extremely severe conditions that did not allowed one to exclude the formation of active rhodium or iridium metal.

In comparison to catalytic processes, stoichiometric hydrodesulfurization or desulfurization reactions of thiophenes are much more numerous and have provided valuable information on the metal-assisted desulfurization mechanism [42]. It is agreed that polynuclear complexes are more suited than mononuclear complexes for the desulfurization of thiophenes [42]. In contrast to heterogeneous HDS, this step seems to occur in fluid-phase systems preferentially through thiolate ligands (hydrogenolysis products).

The desulfurization of BT to ethylbenzene via the dimer $\text{Rh}(\eta^3\text{-}(\text{CO})_5\text{WS}(\text{C}_6\text{H}_4)\text{CH}=\text{CH}_2)(\text{triphos})$ (**I**) in THF is the process which perhaps best illustrates the co-operation of two metal sites in sulfur removal via the hydrogenolysis path (Scheme 18) [43]. The hydrogenation of the 2-vinylthiophenolate complex $\text{Rh}(\eta^3\text{-S}(\text{C}_6\text{H}_4)\text{-}$



Scheme 18.

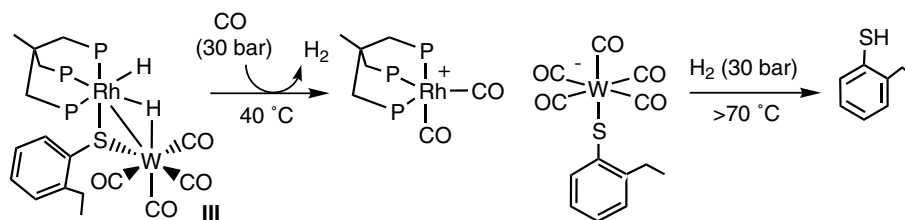
$\text{CH}=\text{CH}_2)(\text{triphos})$ (**II**), obtained by C–S insertion of $[\text{RhH}(\text{triphos})]$ into BT [34], gave selectively free ETP and various rhodium hydride complexes via a (thiolate)dihydride intermediate [32a]. Only when tungsten was incorporated into the complex framework, through a W–S bonding interaction as in complex **I**, hydrodesulfurization occurred with formation of EB and of insoluble tungsten sulfide. Notably, the desulfurization reaction was found to proceed via the intermediacy of the dimer $(\text{triphos})\text{RhH}(\mu\text{-H})(\mu\text{-}o\text{-S}(\text{C}_6\text{H}_4)\text{C}_2\text{H}_5)\text{W}(\text{CO})_4$ (**III**) in which a 2-ethylthiophenolate group and a hydride ligand bridge the metal centers.

Intermediate **III** was intercepted by in situ HPNMR spectroscopy, which also revealed the conditions for its independent preparation. Just the use of isolated **III** allowed one to prove that the cleavage of the S–C bond in the thiolate ligand can also occur as a thermal step with no need of external hydrogen (Scheme 19). It was proposed that the cleavage of the C–S bond is promoted by the bridging hydrogen in **III**. However, it was not clarified whether the mechanism of C–S bond cleavage in the thiolate is either homolytic or heterolytic.

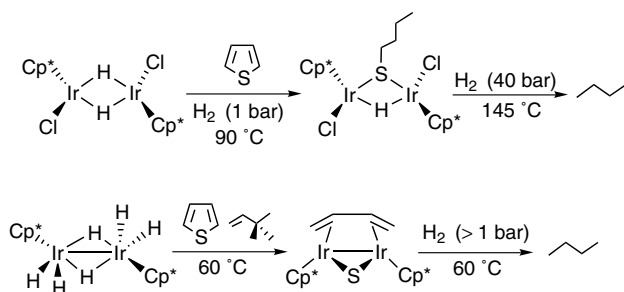
As confirmed by several works, the polymetallic structure of the activating metal complex and the multipoint coordination of thiolates are crucial points for the cleavage of the second C–S bond of thiophenes. In Scheme 20 are illustrated some remarkable examples of stoichiometric HDS of T promoted by the dimer $[\text{IrHClCp}^*]_2$ via a μ -thiolate intermediate [44a] and by the dimer $[\text{IrH}_3\text{Cp}^*]_2$ via a μ -S intermediate [44b].

Valuable mechanistic information on the C–S bond cleavage of thiolate ligands has been provided by the reaction of the cluster $\text{Mo}_2\text{Co}_2\text{S}_3(\text{CO})_4\text{Cp}'_2$ ($\text{Cp}' = \text{CH}_3\text{-C}_5\text{H}_4$) with thiols (Scheme 21) [45a]. The Co/Mo/S cluster desulfurizes thiolates through a mechanism in which the key steps are the creation of coordination vacancies at the promoter cobalt atom, the multipoint (μ^3) coordination of the thiolate group and the homolytic C–S bond cleavage (Scheme 21). Attempts of using $\text{Mo}_2\text{Co}_2\text{S}_3(\text{CO})_4\text{Cp}'_2$ to desulfurize T were partially successful as butane was actually obtained, but the sulfur was incorporated into a new cluster $\text{Mo}_2\text{Co}_2\text{S}_4$ [45b] that did not react further.

With the exception of the desulfurization of T and DBT assisted by $[\text{MH}(\text{triphos})]$ fragments ($\text{M} = \text{Rh}, \text{Ir}$) (see above) [32b,38,41], the evolution of H_2S has been never observed in either catalytic or stoichiometric processes. This has been attributed to the high stability of S-(M) $_n$ ($n > 1$) moieties towards the elimination of S as H_2S . Even greater thermal and chemical stability seem to feature M=S moieties which may form along the desulfurization pathway (indeed, only one example of hydrogenation of M=S to M(H)SH in a metal complex has been reported so far [46]).



Scheme 19.

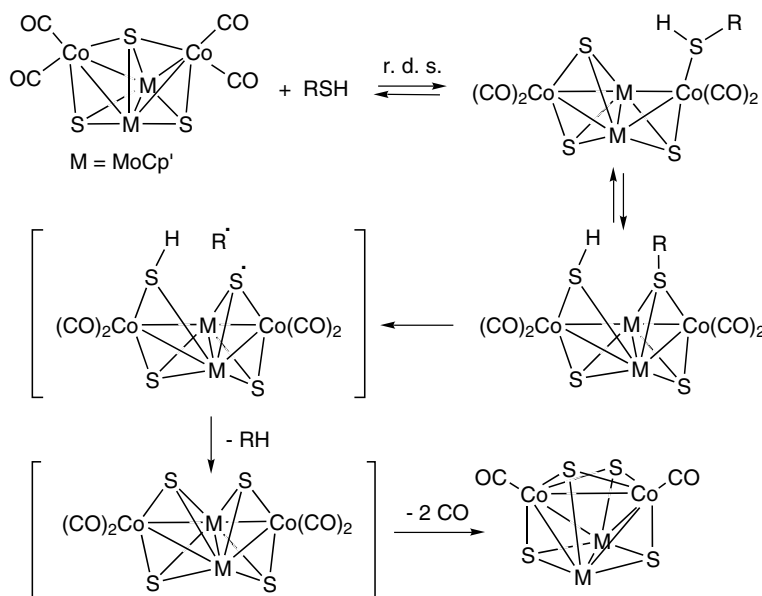


Scheme 20.

10. Heterogeneous desulfurization reactions with molecular catalysts tethered to solid supports

The desulfurization of BT to ethylbenzene (ET) with Rh^{I} -polystyrene (Scheme 16) still represents the first example of heterogeneous HDS of a thiophenic substrate by a single-site metal catalyst. Table 1 reports the data obtained at different times and for two recycles [38].

The surprising HDS of BT by a tethered mononuclear complex has been interpreted in terms of the concomitant action of two metal sites kept in close proximity by the flexible polystyrene matrix (Chart 7).



Scheme 21.

Table 1
Hydrogenation of BT with R^{I} -polystyrene^a

Entry	Time (h)	ETP %	EB %	TON (ET)	Conv. %
1	2	48.5	2.5	97	51.0
2	5	62.2	4.0	124	66.2
3	10	74.3	5.5	349	79.8
4 ^b	2	47.6	3.1	95	50.7
5 ^b	2	48.0	3.5	96	51.5

^a Experimental conditions: 30 ml THF, Rh 3.5×10^{-2} mmol, BT 7 mmol, ^tBuOK 7 mmol, 160 °C, 30 bar H_2 , 1500 rpm; product composition determined by GC/MS after acidification of the catalytic mixture with aqueous HCl.

^b Recycling in the same conditions of entry 1.

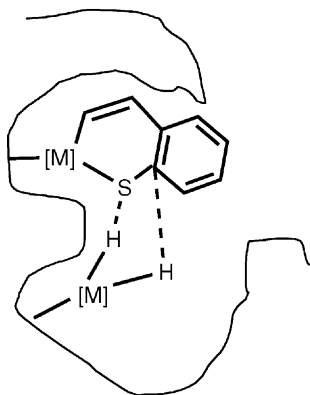


Chart 7.

The cooperation of at least two metal sites to promote the desulfurization of a thiophenic substrate has several precedents in the literature [43,47]. Moreover, the existence of interactions between contiguous metal centers in polystyrene-tethered catalysts, especially at high metal loadings, has been established in a number of catalytic reactions and ascribed to the flexibility of the organic support [48].

11. Conclusions

This review has highlighted the progress achieved over the last 10 years in the field of single-site HDS catalysis, illustrated by selected case studies and important milestones.

The impact of single-site catalyst technology does not reach the frontiers of actual hydrotreating catalysis, yet it can provide some clues to design alternative processes to desulfurize hydrotreated diesel down to low-ppm levels suitable for impending low sulfur fuel regulations. To this purpose, aqueous diphasic catalysis and catalysis with single metal sites supported on both inorganic and organic materials appear as viable technologies. Indeed, the complexity of the HDS process and the many alternative and/or different mechanisms, that many be operative even on the surface of the same catalyst, cannot be realistically reproduced by homogeneous models employing ligands, thiophenes and experimental conditions far away from those applied in industrial catalysis. Nonetheless, it has been shown that many reactions of single metal sites with thiophenes show surprising analogies with related reactions occurring over the surface of HDS catalysts. These analogies and some successful reactions with heterogenized metal precursors are providing the driving force to investigate the HDS process by single-site catalysts.

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