

Hydrogenation, Hydrogenolysis, and Desulfurization of Thiophenes by Soluble Metal Complexes: Recent Achievements and Future Directions

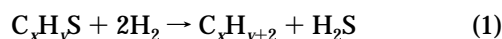
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Hydrodesulfurization Process

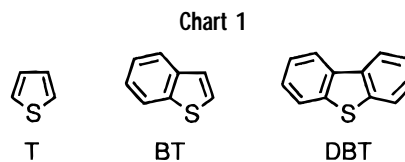
Petroleum and natural gas contain various organosulfur compounds, and their removal by hydrodesulfurization (HDS) over heterogeneous catalysts (eq 1) produces hydrocarbons and H₂S,¹ which may be disposed of as elemental sulfur by the Claus process.²



The HDS process is typically catalyzed by metal sulfides deposited on a support; Mo and W are essential *components*, but increased catalytic activity, particularly toward the thiophenes, is observed when the catalysts comprise also various late transition metals, generally belonging to group 8, that are termed *promoters*.^{1,3} Current technology can adequately desulfurize aliphatic and acyclic sulfur compounds, but it is apparently unsuccessful in treating thiophene and its derivatives to achieve new specifications imposed by recent Clean Air regulations, which require increasingly reduced sulfur contents in fuels as well as the optimum operation of the reforming and cracking plants. Under the combined prod of business pull and environmental push, a great deal of research is thus being paid worldwide to the development of more efficient HDS technologies.

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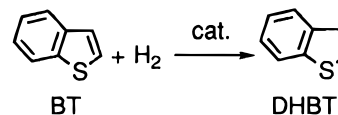
In the development of a new generation of heterogeneous HDS catalysts with improved efficiency, homogeneous modeling studies have substantially contributed to a better understanding of several fundamental aspects related to the interactions with transition metals of thiophenic substrates and of the sulfur compounds derived thereof (e.g., thiols, sulfides). Indeed, many types of reactions between discrete organometallic complexes and thiophenes occur also on the surface of heterogeneous catalysts and the mechanistic understanding obtained in solution has been applied to elucidate surface phenomena.⁴

Some reviews covering the coordination chemistry of thiophenes,^{4h–j} their breaking by metal complexes to give either C–S inserted^{4a–g} or desulfurized products,^{4c,g,h} and their hydrogenation and hydrogenolysis reactions assisted by transition metal complexes^{4a–c} have already appeared. The continuous flourishing of new and interesting results, however, justifies amply the appearance of this Account in which we focus on hydrogenation, hydrogenolysis, and desulfurization reactions of thiophenic substrates by soluble metal complexes, and even within this limited range, attention will be confined to novel aspects and only the most recent breakthroughs. Key references are provided to lead the reader into related areas of interest however.

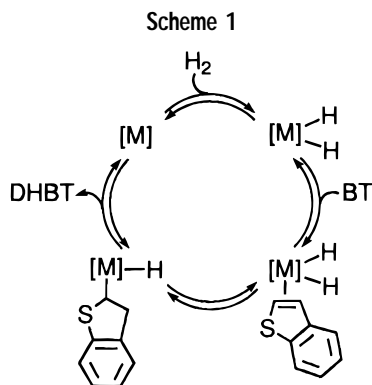
Hydrogenation of Thiophenic Substrates to Cyclic Thioethers with Soluble Metal Catalysts

Of the three model thiophenes that are currently employed in homogeneous studies (Chart 1), benzo[*b*]thiophene (BT) is the most easily hydrogenated to the corresponding thioether, dihydrobenzo[*b*]thiophene (DHBT), in the presence of metal catalysts (eq 2).^{5–7}

The major reactivity of BT has been attributed to the more pronounced “olefinic” character of the C₂–C₃ double bond as compared to thiophene (T) and to the minor aromatic character as compared to dibenzo[*b,d*]thiophene (DBT), of which no example of hydrogenation to either tetrahydrodibenzothiophene or hexahydrodibenzothiophene has been reported so far.



The regioselective hydrogenation of BT to DHBT is catalyzed by several metals, all of them belonging to the class of *promoters* (Ru, Os, Rh, and Ir),^{5–7} under reaction conditions that may be as mild as 40 °C and subambient



H_2 pressure.^{6a,b} The catalytic rates are generally low, however. A general hydrogenation mechanism has been proposed on the basis of deuterium labeling experiments,^{5a} kinetic studies applying gas uptake techniques,^{6a,b} and theoretical methods.^{6b} Consistent with the pseudoolefinic character of the C_2 - C_3 double bond, the catalysis cycle comprises steps that are commonly encountered in metal-catalyzed hydrogenations of alkenes: oxidative addition of H_2 , coordination of BT via the double bond, hydride migration to give 2- or 3-dihydrobenzothiophenyl, reductive coupling of hydride and dihydrobenzothiophenyl ligands, and displacement of DHBT by the substrate (Scheme 1).

Peculiar mechanistic features of the hydrogenation of BT have been demonstrated by Fish via deuterium labeling experiments using $[Cp^*Rh(CH_3CN)_3](BF_4)_2$ as a catalyst precursor (reversibility of the first hydride migration step—possible η^6 -coordination of DHBT)^{5a} and by Sánchez-Delgado via kinetic studies using $[Rh(COD)(PPh_3)_2]PF_6$ (reaction rate determined by the hydride migration that gives the dihydrobenzothiophenyl intermediate).^{6b} From a comparison of the catalytic activities of $[Rh(COD)(PPh_3)_2]PF_6$ and $[Ir(COD)(PPh_3)_2]PF_6$ in different solvents (THF, 2-methoxyethanol, and 1,2-dichloroethane), Sánchez-Delgado and Bianchini have shown that the hydrogenation reactions proceed with the same mechanism but may be retarded (Rh) or even inhibited (Ir) depending on the coordinating properties of the solvent.^{6a,b}

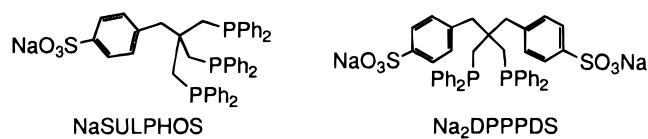
A quite efficient homogeneous catalyst for the regioselective hydrogenation of BT to DHBT has recently been developed in this laboratory using as precatalyst the Ru(II) complex $[(triphos)Ru(CH_3CN)_3]^{2+}$ in THF [triphos = $MeC(CH_2PPh_2)_3$].⁸ The reaction, which already occurs at room temperature, is most likely catalyzed by the fragment $[(triphos)RuH]^+$ (detected during catalysis by high-pressure NMR spectroscopy as DHBT adduct) obtained by heterolytic splitting of H_2 . This Ru(II) system is much more efficient (tof of ca. 30, mol(DHBT) mol(cat)⁻¹ h⁻¹, at 60 °C and 30 atm of H_2) than its Rh(I) analogue $[(triphos)RhH]$ (tof of ca. 1 at 160 °C and 30 atm of H_2) (tof = turnover frequency).^{7b}

In an attempt to apply aqueous biphasic catalysis to the HDS process, particularly to the purification of naphthas, various water-soluble catalysts have recently been designed. At the Venezuelan company INTEVEP S.A., a patent has been filed which describes various water-soluble ruthenium systems capable of catalyzing the

hydrogenation of BT to DHBT in a 1:1 water/decane mixture.⁹ The catalysts are generated in situ by reaction of either *m*-monosulfonated (TPPMS) or trisulfonated triphenylphosphine (TPPTS) with various Ru(II) or Ru(III) precursors. The catalytic rates are generally low (at 69 bar of H_2 and 130 °C, a tof of ca. 2.5 was reported), but they increase significantly in the presence of quinoline or aniline cocatalysts. It is suggested that these nitrogen bases have several beneficial effects on the reaction rate by leading to faster formation and better stabilization of the catalytically active species and to more efficient emulsions as well.

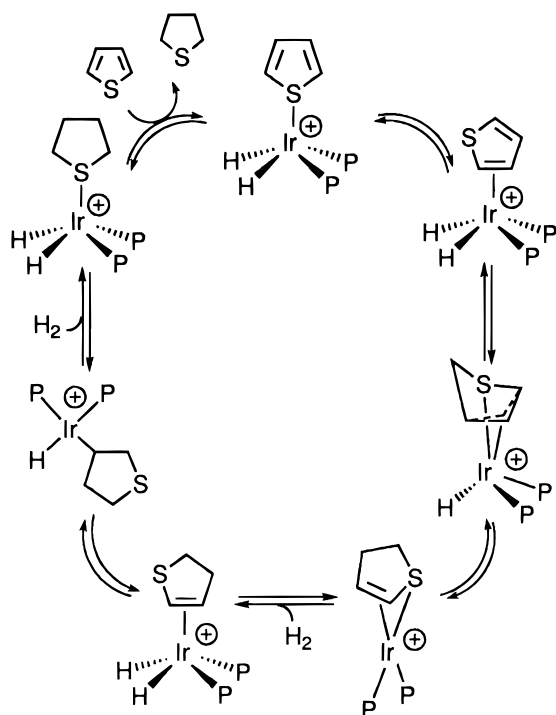
In our laboratory, the challenge of liquid biphasic catalysis applied to HDS has been accepted with the development of Rh and Ru catalysts stabilized by the two water-soluble polyphosphines $NaO_3S(C_6H_4)CH_2C(CH_2PPh_2)_3$ (NaSULPHOS)¹⁰ and $(NaO_3S(C_6H_4)CH_2)_2C(CH_2PPh_2)_2$ (Na₂DPPPDS).¹¹

The Rh(I) zwitterionic complex (SULPHOS)Rh(COD) functions as catalyst precursor for the hydrogenation of BT to DHBT in biphasic systems comprised of water and methanol as polar phase and *n*-heptane as hydrocarbon phase with no need of external surfactants.^{7a} Although the catalyst system is very robust and can tolerate relatively drastic reaction conditions for a long time (30 atm of H_2 , 200 °C), the catalytic activity is quite modest (tof of ca. 2). Under comparable conditions, a much better efficiency is exhibited by the Ru(II) complex $[(SULPHOS)Ru(MeCN)_3]SO_3CF_3$, which catalyzes the hydrogenation of BT to DHBT in H_2O -MeOH/*n*-heptane with a tof of ca. 40 already at 100 °C.⁸ A slightly lower activity has been observed with Na₂DPPPDS in combination with various rhodium and ruthenium salts.⁸ Unlike SULPHOS complexes, the hydrogenation reactions of BT to DHBT with the chelating diphosphine occur in water/hydrocarbon biphasic systems with no need for alcohol cosolvents.



In contrast to the fairly good propensity of T to form η^2 -(C,C) adducts using the double bond adjacent to sulfur,¹² the hydrogenation of T to tetrahydrothiophene (THT) is a rare reaction indeed. The only homogeneous reaction that produces THT in excess of the stoichiometric amounts is that catalyzed by the precursor $[Ir(H)_2(\eta^1-(S)-T)_2(PPh_3)_2]PF_6$ in 1,2-dichloroethane.¹³ Consistent with several reactor studies with commercial HDS catalysts,^{1,3} this hydrogenation reaction is a stepwise process that involves the proven intermediacy of 2,3-dihydrothiophene (Scheme 2). The overall mechanism for the formation of THT is not too dissimilar from that proposed for BT in Scheme 1. A major difference, however, may be seen in the first hydride migration step that gives a thioallyl ligand (stereoselective endo migration to the C_2 carbon atom of η^2 -(C,C)-T). The poor catalytic activity has been attributed

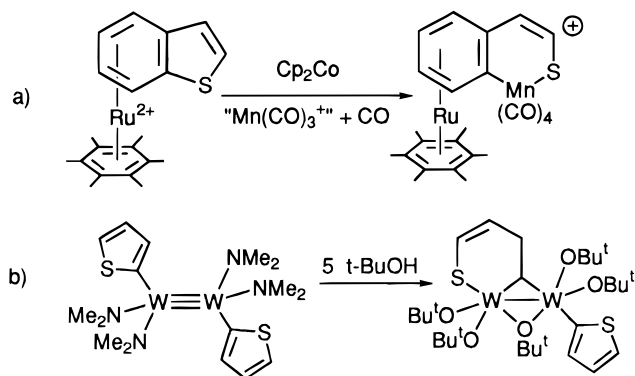
Scheme 2



to the good σ -donor properties of THT. This ligand is not easily displaced by T and ultimately traps all the catalytically active species as the bis-THT complex $[\text{Ir}(\text{H})_2(\eta^1\text{-S-THT})_2(\text{PPh}_3)_2]\text{PF}_6$, which, in fact, is the termination metal product of the catalysis.¹³

In summary, the design of a homogeneous catalyst for the plain hydrogenation of thiophenes requires one to take into consideration a number of specific aspects. First of all, one has to consider that, unlike alkenes, BT and T are polyfunctional ligands which can bind metal centers in a variety of bonding modes, often in a rapid equilibrium with each other.^{4d-j,14} Among the possible coordination modes, the $\eta^1\text{-S}$ and the $\eta^2\text{-C,C}$ ones are the most common and also the most important to direct the following reactivity of the coordinated thiophene toward H_2 . The $\eta^2\text{-C,C}$ bonding mode, which is propoedeutical to hydrogenation, is more sterically demanding than the $\eta^1\text{-S}$ bonding mode (the immediate precursor to C–S bond cleavage)^{15d,e} even in the absence of substituents in the thiophene. When BT or T bears substituents, its hydrogenation to thioethers is thwarted,¹ and indeed, no example of homogeneous hydrogenation of substituted thiophenes has ever been reported. It is therefore anticipated that bulky metal fragments are poor hydrogenation catalysts, while they may be effective catalysts for the hydrogenolysis of thiophenes (*vide infra*).^{7,16} In a similar way, a great basicity at the metal center is not required for an effective hydrogenation catalyst as it may favor C–S bond cleavage (hence hydrogenolysis pathways) via transfer of electron density from a filled metal orbital of appropriate symmetry into a σ^* C–S orbital (generally the $\text{C}_2\text{-S}$).^{4,15d,e} Ultimately, the most critical feature for a successful hydrogenation catalyst would be that of having a low thiophilicity to disfavor both $\eta^1\text{-S}$ coordination of

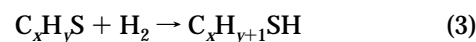
Scheme 3



the incoming thiophene and the formation of stable adducts with the thioether products. Consistent with the relevant reports in the literature, ideal candidates are Ru(II) fragments with moderate steric crowding.

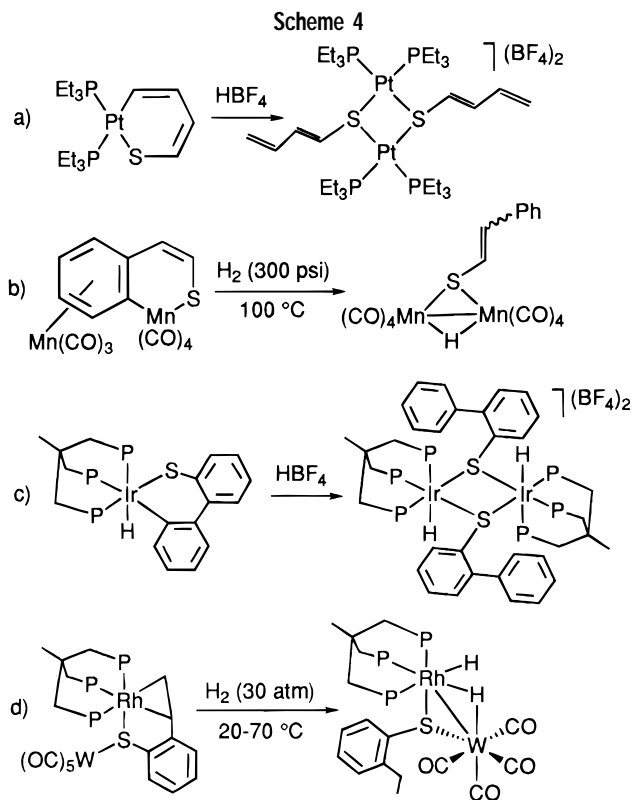
Hydrogenolysis of Thiophenic Substrates to Thiols with Soluble Metal Catalysts

The hydrogenolysis of thiophenes to thiols is a reaction of much relevance in the HDS process (eq 3). In particular, the thiols, like the thioethers, can efficiently be desulfurized over conventional catalysts under milder reaction conditions than those required to accomplish the HDS of the thiophene precursors.^{1,3}



Ring opening of thiophenes can be achieved in several different ways that have extensively been reviewed.⁴ Most common procedures involve either the direct interaction of electron-rich metal metal fragments with the desired thiophene (e.g., [(triphos)MH] (M = Rh, Ir),^{7,16,17} $[\text{Cp}^*\text{Rh}(\text{PMe}_3)]$,¹⁵ $[\text{Pt}(\text{PET}_3)_3]$,¹⁸ $[\text{Fe}(\text{dmpe})_2]$,¹⁹ $[\text{Ir}(\text{PMe}_3)_3]^+$,²⁰ $[\text{Cp}_2\text{W}]$,²¹ or $[\text{Tp}^*\text{Rh}(\text{PMe}_3)]$ ²²) or the addition of nucleophiles²³ or electrophiles²⁴ to $\eta^4\text{-}$ and $\eta^5\text{-}$ thiophene complexes. Alternative strategies for C–S bond scission have recently been reported by Sweigart²⁵ and Chisholm.²⁶ The first author has shown that the activation of the carbocyclic ring of BT by an appropriate metal fragment (e.g., $[\text{Mn}(\text{CO})_3]^+$ or $[\text{Ru}(\text{C}_6\text{Me}_6)]^{2+}$) can favor the regioselective insertion of an electron-rich fragment (e.g., $\text{Mn}(\text{CO})_4$) into the S–C_{aryl} bond (Scheme 3a),²⁵ which is a quite unusual reaction unless BT is substituted in the 2-position.^{15b} Chisholm has shown that the cooperation of two metal centers can promote the opening of 2-thienyl ligands (but not of 3-thienyl ligands) in such a way that the carbon atom of the C–S inserted thiophene bridges two metal centers (Scheme 3b).²⁶

Unlike C–S insertion, the conversion of metallathia-cycles to thiolato complexes via M–C bond cleavage, followed eventually by the formation of free thiols, is a quite rare reaction occurring both stoichiometrically and catalytically. Stoichiometric reactions proceed via either protonolysis^{18,27} or hydrogenation of metallathia-cycles.^{25b,28,29} Selected examples are illustrated in Scheme 4 for T,^{18a}



BT,^{25b,28} and DBT.²⁷ In most instances, the products are dimers in which the thiolate ligands bridge two metal centers.

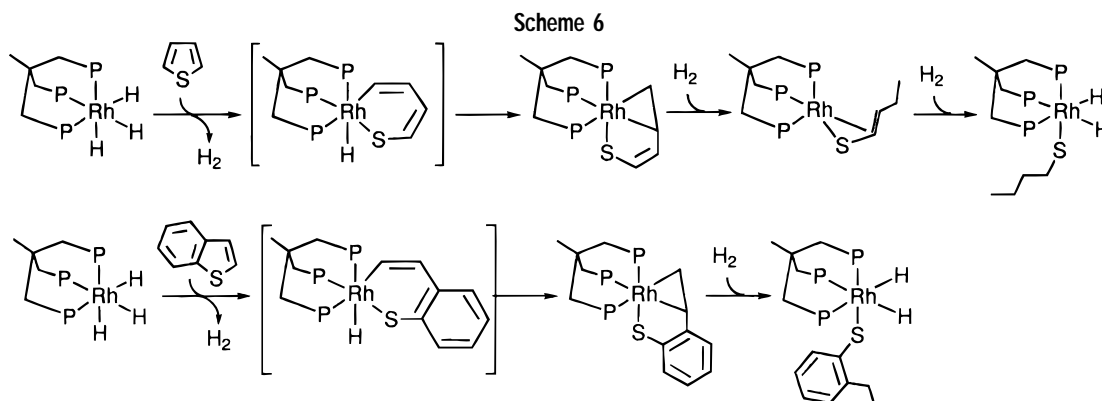
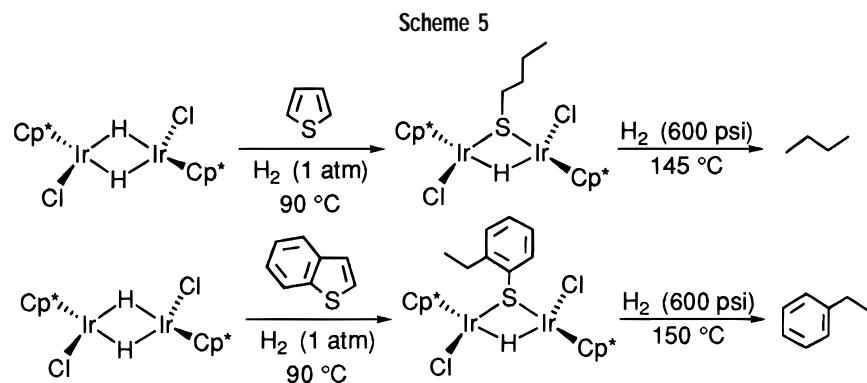
One-pot hydrogenolysis, followed by desulfurization, has recently been observed by Vicic and Jones using the dimer $[\text{Cp}^*\text{IrHCl}]_2$, which reacts with T and BT in the

presence of H_2 to give $[\text{Cp}^*\text{IrCl}]_2(\mu\text{-H})(\mu\text{-SC}_4\text{H}_9)$ and $[\text{Cp}^*\text{IrCl}]_2(\mu\text{-H})(\mu\text{-S}(\text{C}_6\text{H}_4)\text{CH}_2\text{CH}_3)$, respectively (Scheme 5).^{29a} A mechanism has been proposed in which both the C–S bond cleavage of the thiophene and the hydrogenation of the unsaturated thiolate is brought about by a mononuclear species derived from the fragmentation of $[\text{Cp}^*\text{IrHCl}]_2$. The remaining Ir fragment, $[\text{Cp}^*\text{IrH}(\text{Cl})]$, stabilizes the hydrogenolysis products and ultimately contributes to form the dimers which can be desulfurized upon thermolysis under a high pressure of H_2 .

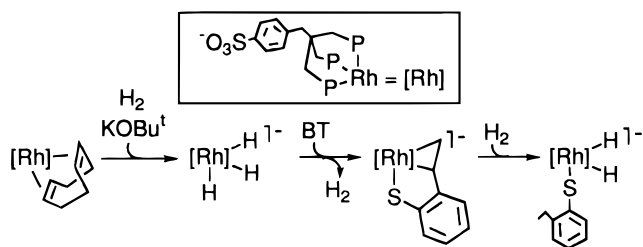
Catalytic examples of hydrogenolysis of thiophenic substrates are known exclusively for the $16e^-$ species $[(\text{triphos})\text{MH}]$ ($\text{M} = \text{Rh}^{7,16a,b}$ and Ir^{16c}) generated in situ by either thermolysis of appropriate precursors^{7b,16c} or base-assisted heterolytic splitting of H_2 (e.g., $[\text{M}]^{n+} + \text{H}_2 + \text{base}^- \rightarrow [\text{M-H}]^{(n-1)+} + \text{baseH}$).^{7a,16a,b} For kinetic reasons, the Rh fragment is more active than the Ir analogue and effectively catalyzes the hydrogenolysis of T,^{16a} BT,^{7,16a} DBT,^{16a} and dinaphtho[2,1-*b*:1',2'-*d*]thiophene^{16b} to the corresponding thiols in common organic solvents under relatively drastic conditions (160 °C, 30 atm of H_2). The capability of triphos complexes to tolerate reaction temperatures as high as 200 °C with no substantial decomposition and the high energy of the $16e^-$ fragments $[(\text{triphos})\text{MH}]$ are important factors in ensuring catalytic activity.

Typical reaction sequences that transform thiophenes into thiolate ligands by action of $[(\text{triphos})\text{RhH}]$ and H_2 are shown in Scheme 6.

Substitution of NaSULPHOS for triphos in combination with a strong Brønsted base has allowed us to perform the hydrogenolysis of BT to 2-ethylthiophenol (ETP) by



Scheme 7



rhodium catalysis in liquid biphasic systems comprising *n*-heptane as hydrocarbon phase and water or methanol as polar phases.^{7a} As is shown in Scheme 7, the chemistry of the catalyst precursor (SULPHOS)Rh(COD) employed in the liquid biphasic reactions is quite similar to that of the triphos analogue.

Irrespective of the phase variation and of the thiophenic substrate, it has been observed that the hydrogenolysis rates with either [(triphos)RhH] or [(SULPHOS)RhH]⁻ increase remarkably by addition of strong Brønsted bases (e.g., NaOH) in concentrations approximately equal to those of the substrates.^{7a,16a} This beneficial effect has been attributed to the positive influence exerted by the base on the rate-determining step, i.e., the reductive elimination of the thiol from the metal center (vide infra). In the base-assisted reactions, the hydrogenolysis products are recovered as sodium or potassium thiolates which can either be converted to thiols by acidification with protic acids or be oxidized to disulfides by exposure to air.^{7a,16a} In turn, all of the Rh catalyst of the aqueous biphasic reactions remains in the polar phase for use in a further catalytic run after the thiolate product is extracted as thiol.

The combined information gathered from kinetic studies,^{7a} in situ high-pressure NMR experiments,^{7,16a,b} and the isolation of intermediates related to catalysis leads to a common mechanism for all the hydrogenolysis reactions of T, BT, DBT, or other thiophenes catalyzed by triphos or SULPHOS rhodium complexes in conjunction with strong Brønsted bases. This mechanism, illustrated in Scheme 8 for the model substrates BT (a) and T (b),

involves the usual steps of C–S insertion, hydrogenation of the C–S inserted thiophene to the corresponding thiolate, and base-assisted reductive elimination of the thiol to complete the cycle (in the catalytic reactions carried out in the absence of base, the displacement of the thiol by the substrate occurs thermally).^{7,16}

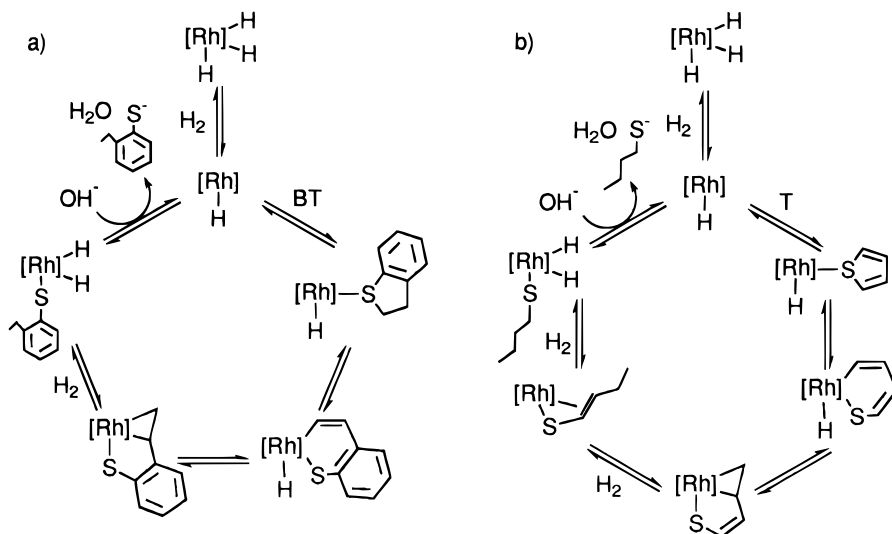
Desulfurization of Thiophenic Substrates to Hydrocarbons with Soluble Metal Complexes

Homogeneous reactions leading to desulfurization of thiophenes have recently been reviewed.^{4c,8} In analogy to heterogeneous HDS, it has been concluded that the degradation to H₂S (or M=S) and hydrocarbons may be achieved in solution using either polynuclear species or external sources of “activated” hydrogen atoms. In particular, the presence of more than one metal seems to be of mandatory importance for the cleavage of the remaining C–S bond after the first one has been C–S inserted.

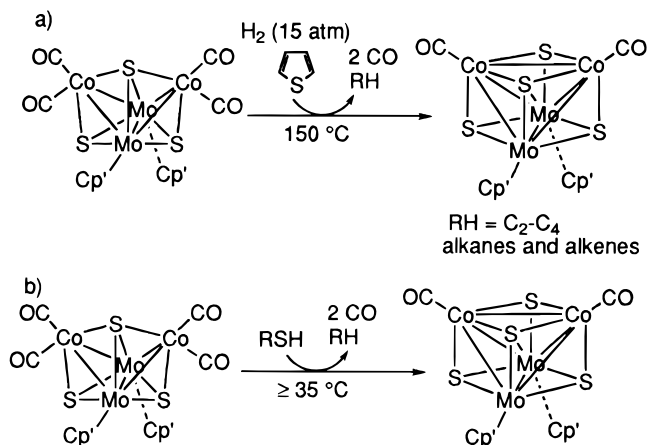
Recent examples of desulfurization of thiophenes by polynuclear complexes have been reported by Curtis,³⁰ Angelici,³¹ Rauchfuss,³² Jones,²⁹ and Bianchini.²⁸ Among these, the overall degradation of T assisted by the cluster Cp'₂Mo₂Co₂S₃(CO)₄ (Cp' = CH₃C₅H₄) is the model reaction that, in our opinion, best resembles the heterogeneous counterparts, particularly those classified as “Co/Mo/S” phase,^{1a} in terms of both structural motif and HDS activity (the hydrogen atoms necessary for the hydrogenolysis step are in fact externally added and not already incorporated into the organometallic precursor) (Scheme 9a).^{30b} Moreover, the Co/Mo/S cluster has successfully been employed to show that the C–S bond scission in the desulfurization of aromatic and aliphatic thiols occurs in homolytic fashion at 35 °C and that thiolate and sulfido groups can move over the face of the cluster as they are supposed to do over the surface of heterogeneous catalysts (Scheme 9b).^{30a}

The combined information gathered from the desulfurization reactions of T and thiols by Cp'₂Mo₂Co₂S₃(CO)₄ has led Curtis and co-workers to propose a new mecha-

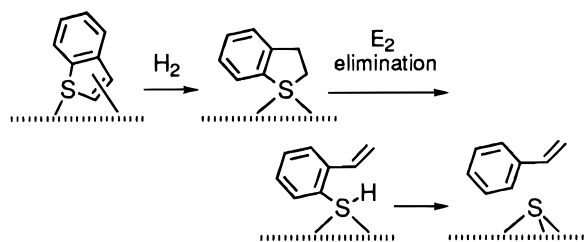
Scheme 8



Scheme 9



Scheme 10



nism for the HDS of thiophenes over “Co/Mo/S” catalysts.³⁰ This mechanism is exemplified in Scheme 10 for BT and involves hydrogenation of the C_2-C_3 double bond, formation of 2-vinylthiophene by an E_2 elimination, and hydrocarbon elimination by homolysis of the $S-C_{\text{aryl}}$ bond. This pathway rationalizes the primary formation of DHBT observed in some HDS reactions of BT over “Co/Mo/S” catalysts as well as the kinetic evidence that the rate-determining step on real catalysts is the removal of surface sulfur.^{1,3}

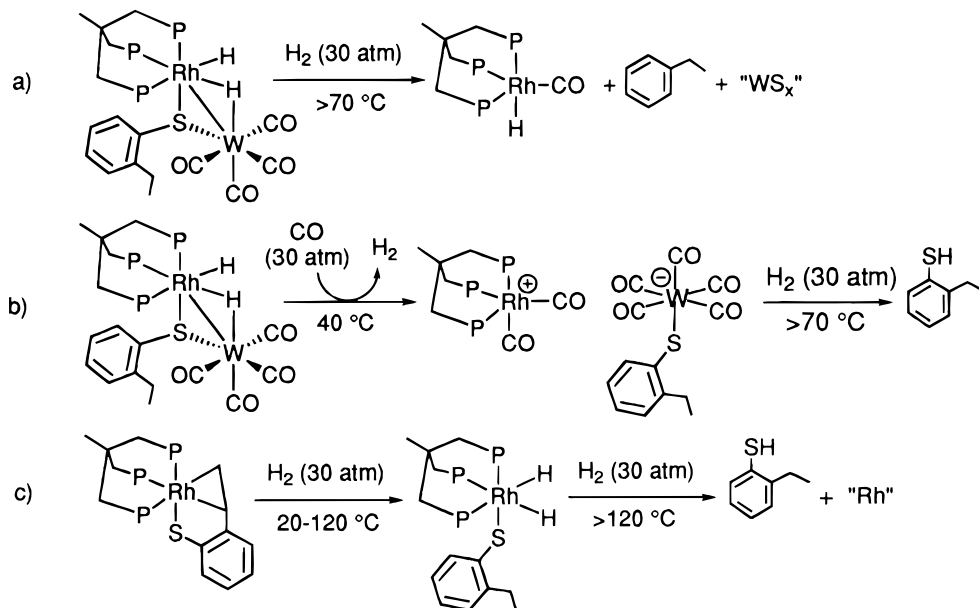
Both the cooperation of *component* and *promoter* metals in the desulfurization step of BT to ethylbenzene

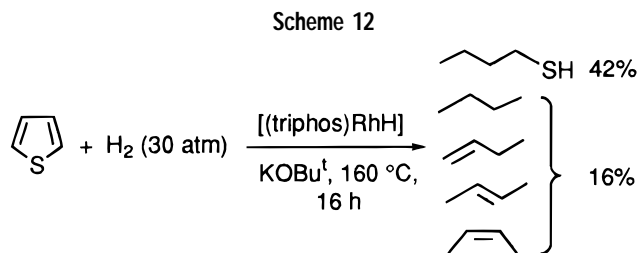
and the walking of thiolate groups from one metal to another have recently been observed to take place in the reactions of the BT-derived heterometal dimer (triphos)- $RhH(\mu-H)(\mu-o-S(C_6H_4)CH_2CH_3)W(CO)_4$ with H_2 and CO, respectively (Scheme 11a,b).²⁸ Most importantly, in the absence of the W *component*, (triphos) $Rh[\eta^3-S(C_6H_4)-CH=CH_2]$ reacts with H_2 under comparable conditions undergoing M–C cleavage but not S–C cleavage (Scheme 11c),^{7b} while in the absence of the Rh *promoter*, $[W(CO)_4-(S(C_6H_4)CH_2CH_3)]^-$ undergoes M–S cleavage but not S–C cleavage (Scheme 11b).^{28a} In light of these findings, it was concluded that the major activity of promoted catalysts in the HDS of BT might also be due to the ability of *promoter* metals to favor hydrogenolysis pathways due to the lower energy barrier to C–S insertion as compared to *component* metals.

The notion that the formation of a μ -thiolato bridge may be important in cleaving both C–S bonds in thiophenes has also been confirmed by Vicic and Jones, who have shown that T and BT are desulfurized to butane and ethylbenzene by treatment of the hydrogenolysis intermediates $[Cp^*IrCl]_2(\mu-H)(\mu-SC_4H_9)$ and $[Cp^*IrCl]_2(\mu-H)(\mu-S(C_6H_4)CH_2CH_3)$ with H_2 (600 psi) at $150\text{ }^\circ\text{C}$, respectively (Scheme 5).^{29a}

In contrast to hydrogenation and hydrogenolysis, no catalytic desulfurization reaction of thiophenes by soluble metal complexes has ever been shown to take place through a clear and unambiguous homogeneous process. A few examples of “seeming” homogeneous HDS of DBT and T have been reported, however. Some years ago, we showed that the DBT C–S insertion product (triphos) $IrH(\eta^2-(C,S)\text{-DBT})$ reacts in THF with DBT under 30 atm of H_2 at $160\text{ }^\circ\text{C}$ to give biphenyl and H_2S in excess of the stoichiometric amounts.^{16c} More recently, catalytic production of butane, butenes, and H_2S has been observed upon hydrogenation (30 atm of H_2) of T in the presence of the [(triphos) RhH] catalyst generated in situ by different

Scheme 11





ways and of a strong base (Scheme 12).^{16a} Both of these reactions are reproducible and also occur in the presence of large excesses of elemental mercury; nonetheless we are still reluctant to consider them as true homogeneous processes, although we have not been able to demonstrate their heterogeneous nature, either.

To summarize, polynuclear complexes, eventually containing both *component* and *promoter* metals, are more suited than mononuclear species for the catalytic HDS of thiophenes by soluble metal complexes. The fact that all the known attempts with polynuclear species have failed in assisting a catalytic reaction is probably due to the great stability of the M=S and M–S–M' moieties toward the elimination of S as H₂S. Indeed, the first example of hydrogenation of M=S to M(H)SH in a discrete homogeneous metal system has been reported only in 1997 by Bergman and co-workers for Cp*₂TiS(pyridine).³³

Concluding Comments

In this Account, we have attempted to outline what are the optimum electronic and structural characteristics of soluble metal catalysts for the hydrogenation, hydrogenolysis, and hydrodesulfurization of thiophenic molecules. Although, the spectator ligands in the homogeneous modeling studies are not representative of the pool of ligands available to the industrial catalysts, a number of reactions in solution do occur also over the surface of commercial HDS catalysts with analogous mechanisms. Besides the contribution to rational catalyst development, homogeneous studies are serving also to define alternative strategies for the purification of naphthas and gas oils. HDS via aqueous biphasic catalysis or via supported liquid-phase catalysis are already industrial prospects for improving fuel quality. An exciting future direction which is under serious consideration is the transformation of thiophenes into water-soluble derivatives, as sulfones or hydroxy-substituted derivatives, via chemical or electrochemical oxidation.

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