Hydrogenation and hydrogenolysis of thiophenic molecules catalysed by soluble metal complexes†

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In this review are discussed the known hydrogenation and hydrogenolysis reactions of thiophenic molecules catalysed by soluble metal complexes. Homogeneous desulfurization reactions are also briefly summarized. The mechanistic information provided by the homogeneous modelling studies is critically evaluated through comparisons with the surface reactions that have been proposed to be implicated in the heterogeneous hydrodesulfurization catalysis.

The hydroprocessing of petroleum represents one of the largest scale chemical processes carried out by industry in the world today. In this procedure, crude oil is treated with hydrogen at high pressure (150–3000 lbf in^{-2}) over a hot heterogeneous catalyst (Co- or Ni-promoted Mo or W sulfides supported on Al_2O_3) (500–825 °C) to remove nitrogen, sulfur and residual metals prior to further processing.[1] The removal of sulfur from residues in oil is commonly referred to as hydrodesulfurization (HDS) [equation (1)].

$$C_xH_yS + 2\,H_2 \longrightarrow C_xH_{y+2} + H_2S \qquad (1)$$

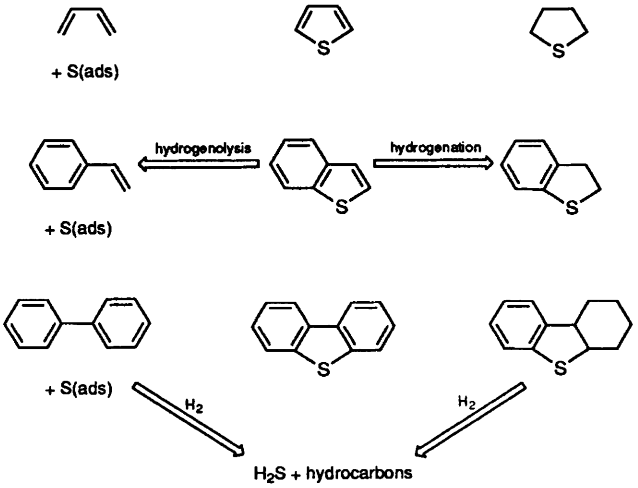
Since new drilling techniques allow the recovery of heavier crude oils that contain higher levels of sulfur, removal of this element is becoming even more important, particularly for those countries that possess very large proven reserves of heavy crudes.

There are two major reasons for reducing sulfur levels in petroleum feedstocks: (*i*) to minimize the amounts of sulfur oxides introduced into the atmosphere by combustion of petroleum-based fuels (contribution to acid rain) and (*ii*) to prevent poisoning of reforming and cracking catalysts that are used to upgrade feedstocks to product fuels.

Recent environmental pollution regulations require lower amounts of sulfur in fuels which cannot be achieved using known technology; thus there is increasing interest in developing new catalysts and processes for the removal of sulfur from the organosulfur compounds in petroleum.

Despite the evident importance of HDS, the mechanism of this reaction is far from being fully elucidated, particularly as regards the activation of thiophenes, benzothiophenes and dibenzothiophenes which, among the sulfur residues in oil, are the most difficult to desulfurize.[2] The principal mechanisms proposed for the heterogeneous HDS of thiophenes are summarized in Scheme 1.

The lack of a deep mechanistic knowledge of the HDS process constitutes a serious limit to the design of improved catalysts. Indeed, while many metals are more active as HDS promoters than cobalt or nickel (Ru > Os > Rh ⩾ Ir > Re > Pt > ⩾ Pd > Co ⩾ Ni)[3] molybdenum–cobalt (or nickel) mixtures are still the metals of choice for industrial use. For this reason, a great deal of fundamental work is presently being carried out in order to try to understand the salient features of the HDS process.



Scheme 1

Studies range from those trying to identify intermediates under actual reactor conditions with industrial catalysts,[4] to surface studies of the interaction of thiophenes with clean and sulfided metal surfaces,[5] to homogeneous modelling of the types of steps that may be involved in the industrial catalyst system.[6] The homogeneous modelling approach, which is amenable to mechanistic studies applying spectroscopy in solution, has recently provided a number of important breakthroughs. These include: (*i*) the identification of several bonding modes of thiophenes to metal centres;[6] (*ii*) the discovery of various mechanisms by which thiophenes, once activated by the metal, are subsequently cleaved[7–13] and, eventually, desulfurized;[14–24] and (*iii*) the achievement of catalytic reactions leading to either hydrogenation or hydrogenolysis of the thiophenes.[25–27]

While the first two issues of modelling the HDS reaction have been covered by some recent reviews,[6] a comprehensive outlook of the catalytic aspects is still lacking. Here, we have tried to provide an up-to-date review of the catalytic hydrogenation and hydrogenolysis reactions of thiophenic molecules as well as a critical evaluation of the homogeneous results that are most pertinent to the heterogeneous HDS process.

Catalytic Hydrogenation Reactions

The development of efficient catalysts for the plain hydrogenation of thiophenes remains an important goal in HDS chemistry. In fact, the cyclic thioether products can subsequently be desulfurized over conventional HDS catalysts

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† *Non-SI units employed:* lbf in^{-2} ≈ 6895 Pa, atm ≈ 10^5 Pa, cal = 4.184 J, e.u. = 4.184 J K^{-1} mol^{-1}.

Table 1 Homogeneous hydrogenation of benzo[*b*]thiophene

Catalyst	Solvent*	T/°C	P_{H_2}/ atm	10[C_8H_6S]/ mol dm^{-3}	10^3[cat.]/ mol dm^{-3}	Initial rate/ mmol product (mmol catalyst)$^{-1}$ h^{-1}	Ref.
[$Rh(cod)(PPh_3)_2]PF_6$	thf	170	110	1.3	2.4	6.23 ± 0.38	26(*a*)
[$RuCl_2(PPh_3)_3$]	Toluene	170	110	1.3	2.4	6.14 ± 0.37	26(*a*)
[$RuCl_2(PPh_3)_3$]	Benzene	85	21	0.5	5.0	0.3	27(*b*)
[$Ir(cod)(PPh_3)_2]PF_6$	thf	170	110	1.3	2.4	5.02 ± 0.12	26(*a*)
[$RhCl(PPh_3)_3$]	Toluene	170	110	1.3	2.4	3.79 ± 0.09	26(*a*)
[$RhCl(PPh_3)_3$]	Benzene	85	21	0.5	5.0	0.7	27(*a*)
[$OsH(Cl)(CO)(PPh_3)_3$]	Toluene	170	110	1.3	2.4	2.56 ± 0.05	26(*a*)
[$RuH(Cl)(CO)(PPh_3)_3$]	thf	170	110	1.3	1.2	2.21 ± 0.12	26(*a*)
[$Rh(Cp^*)(MeCN)_3][BF_4]_2$	Dichloromethane	40	34	0.66	3.3	0.7	27(*c*)
[$Rh\{\eta^3\text{-}S(C_6H_4)CH{=}CH_2\}(triphos)$]	Acetone	160	30	4.6	4.6	0.6	25(*c*)

* thf = Tetrahydrofuran.

under milder reaction conditions than those necessary to accomplish the hydrodesulfurization of the thiophene precursors.[28] This aspect is particularly important for the benzothiophenes and dibenzothiophenes because the conventional catalysts can desulfurize the corresponding cyclic thioethers, dihydrobenzothiophene and hexahydrodibenzothiophene, without affecting the benzene rings, necessary to preserve a high octane number.

Several homogeneous hydrogenation reactions of the model substrate benzo[*b*]thiophene to dihydrobenzothiophene have been carried out over the last twelve years.[25c,d,26,27] Only one report deals with the hydrogenation of thiophene to tetrahydrothiophene,[25a] while no example of the hydrogenation of dibenzo[*b*,*d*]thiophene has been reported so far.

While the hydrogenation of dibenzo[*b*,*d*]thiophene is evidently made difficult by the remarkable aromatic character of the fused-ring system, the prevalence in fact of hydrogenation reactions of benzo[*b*]thiophene over thiophene is interpreted in terms of the more pronounced 'olefinic' character of the C^2–C^3 bond in the former heterocycle.[29]

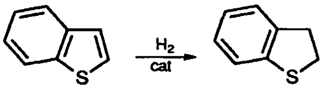
Benzo[*b*]thiophene

The regioselective hydrogenation of benzo[*b*]thiophene to dihydrobenzothiophene (Scheme 2) in homogeneous phase has primarily been reported by Fish *et al.* in 1984.[27a] Since then a variety of soluble transition-metal complexes have been reported to catalyse this reaction, these include [$RhCl(PPh_3)_3$],[26a,27a] [$RuCl_2(PPh_3)_3$],[26a,27b] [$Rh(cod)(PPh_3)_2]PF_6$ (cod = cycloocta-1,5-diene),[26a][$Ir(cod)(PPh_3)_2]PF_6$,[26a][$OsH(Cl)(CO)(PPh_3)_3$],[26a] [$RuH(Cl)(CO)(PPh_3)_3$][26a] and [$Rh(Cp^*)(MeCN)_3][BF_4]_2$ (Cp* = pentamethylcyclopentadienyl).[27c] More recently, catalytic conversion to dihydrothiophene has also been observed as a minor side reaction in the hydrogenolysis of benzo[*b*]thiophene to 2-ethylthiophenol assisted by [$Rh\{\eta^3\text{-}S(C_6H_4)CH{=}CH_2\}(triphos)$] [triphos = $MeC(CH_2PPh_2)_3$].[25c] This reaction, however, will be discussed later.

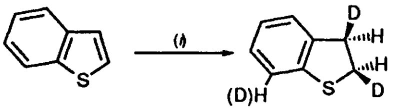
The reaction conditions and the results obtained are summarized in Table 1. Although these data are rather unhomogeneous, one may nevertheless draw some conclusions. (*i*) Drastic reaction conditions are required to accomplish the hydrogenation of benzo[*b*]thiophene with acceptable rates {catalysts [$RuCl_2(PPh_3)_3$] and [$RhCl(PPh_3)_3$]}; (*ii*) at comparable donor-atom sets of the catalyst precursor, the hydrogenation activity increases in the order $Ir \leqslant Rh < Ru \leqslant Os$, which is not far away from the trend observed for the heterogeneous HDS of dibenzo[*b*,*d*]thiophene.[3]

Mechanistic studies on the regioselective hydrogenation of benzo[*b*]thiophene, using [$Rh(Cp^*)(MeCN)_3][BF_4]_2$, [$Rh(cod)(PPh_3)_2]PF_6$ and [$Ir(cod)(PPh_3)_2]PF_6$ as catalyst precursors, have recently been carried out.

The substitution of deuterium for hydrogen gas in the reduction of benzo[*b*]thiophene catalysed by [$Rh(Cp^*)(MeCN)_3][BF_4]_2$ (Scheme 3) has provided information on several of the mechanistic aspects of the reaction:[27d] (*i*) η^2-C^2,C^3 co-ordination of benzo[*b*]thiophene to Rh^{III}) kinetically controls the stereoselective *cis* deuteriation of the double bond; (*ii*) the reduction of the double bond is slightly reversible as trace amounts of deuterium are found in the 2,3-positions of the unreacted benzo[*b*]thiophene; (*iii*) η^6-co-ordination of the thiophene *via* the arene ring of dihydrobenzothiophene occurs most likely after hydrogenation of the C^2–C^3 double bond as minor amounts of deuterium are also incorporated into the 7-position of the dihydrobenzothiophene produced.



Scheme 2



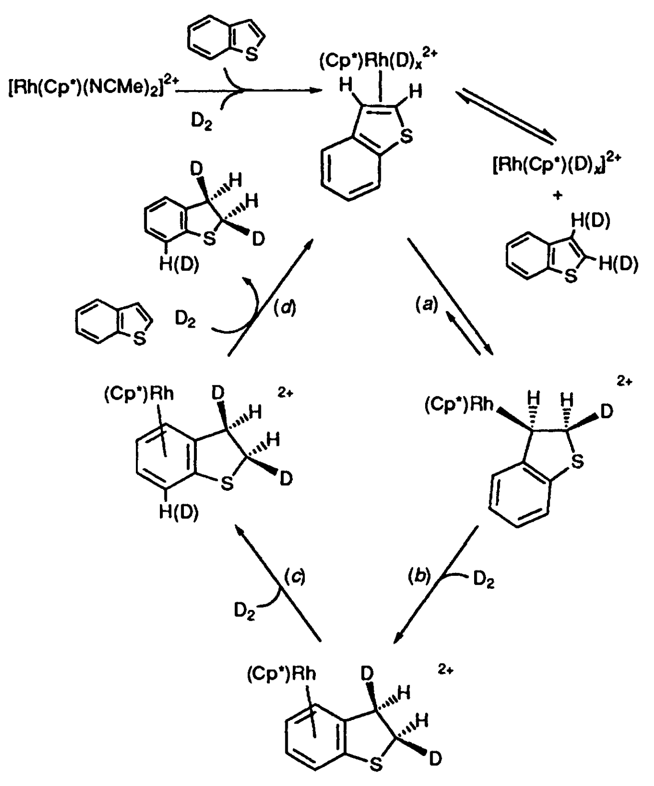
Scheme 3 (*i*) D_2 (500 lbf in^{-2}), [$Rh(Cp^*)(MeCN)_3]^{2+}$, CH_2Cl_2, 40 °C, substrate : catalyst ratio 20 : 1

The mechanism postulated by Fish *et al.*[27d] for this selective transformation of benzo[*b*]thiophene is shown in Scheme 4.

The catalytic cycle starts with the co-ordination of benzo[*b*]thiophene in the η^2-C^2,C^3 fashion to a rhodium polyhydrido species, followed by hydride transfer from the metal to the C^2 carbon atom of benzothiophene [step (*a*)]. Reaction of the resulting 3-dihydrobenzothienyl intermediate with further H_2 gives dihydrobenzothiophene [step (*b*)] that is finally displaced by the benzo[*b*]thiophene substrate [step (*d*)]. The intermediacy of an η^6-arene, preceding this elimination step, is suggested by the observed incorporation of deuterium in the 7-position of dihydrobenzothiophene [step (*c*)].

The absence of a precise stoichiometry (with particular regard to the steps involving the addition of H_2) as well as the ambiguous oxidation state of the metal along the catalysis cycle constitute weak points of the mechanism suggested by Fish *et al.*[27d] In actuality, if the various reactions of H_2 proceed (as apparently accepted by the authors) by oxidative-addition pathways, hypervalent Rh^V) species would be involved in the catalysis, which is quite surprising for rhodium-catalysed hydrogenation reactions of double bonds. Indeed, alternative activation paths of H_2 such as the heterolytic splitting into Rh–H and H^+ species[5c,30] or the dihapto co-ordination mode (η^2-H_2)[31] may well account for this hydrogenation reaction in acetonitrile.

By a combination of kinetic, chemical and theoretical methods and using [$Rh(cod)(PPh_3)_2]PF_6$ as the catalyst precursor Sánchez-Delgado *et al.*[26c] have provided further insight into the mechanism of the homogeneous hydrogenation of benzo[*b*]thiophene to dihydrobenzothiophene in 2-methoxyethanol. In particular, the experimental rate law is $d[C_8H_8S]/dt = k_{cat}[Rh][H_2]$, with k_{cat}(25 °C) = 1.24×10^{-4} $dm^3\ mol^{-1}\ s^{-1}$. The activation parameters are $E_a = 20.7$ kcal mol^{-1}, $\Delta H^‡ = 20.1$ kcal mol^{-1} and $\Delta S^‡ = -11.1$ e.u.



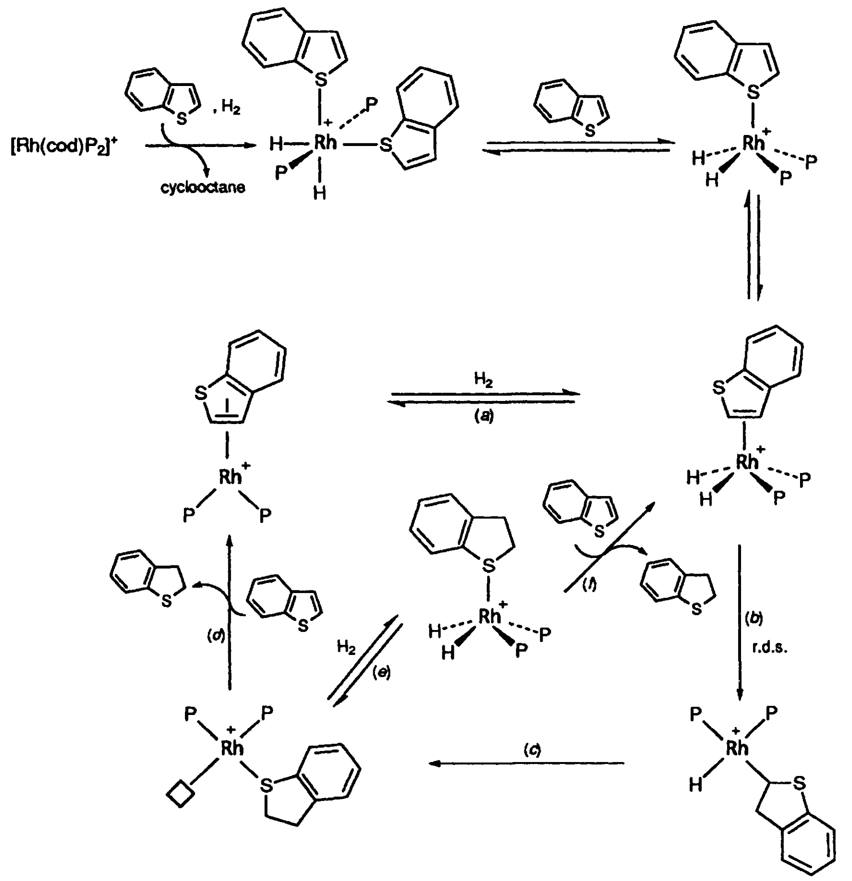
Scheme 4

In the proposed catalytic mechanism (Scheme 5), an active species is the π-complex $[Rh(\eta^5\text{-}C_8H_6S)(PPh_3)_2]^+$ which is in equilibrium with the product resulting from the oxidative addition of H_2, $[RhH_2(\eta^2\text{-}C^2,C^3\text{-}C_8H_6S)(PPh_3)_2]^+$ [step (*a*)]. The rate-determining step (r.d.s.) of the catalytic reaction is the migration of one of the terminal hydrides from the metal to the C^2 carbon atom of the dihapto-bonded benzo[*b*]thiophene ligand to give the (2-benzothienyl)hydride intermediate $[RhH(\sigma\text{-}C_8H_7S)(PPh_3)_2]^+$ [step (*b*)]. The reductive coupling between the remaining hydride and the thienyl ligand then gives a $\sigma\text{-}SC_8H_8$ unsaturated complex which either reacts with benzothiophene to restore the $\eta^5\text{-}C_8H_6S$ complex [step (*d*)] or adds H_2 to give $[RhH_2(\sigma\text{-}SC_8H_8)(PPh_3)_2]^+$ [step (*e*)]. The latter complex finally liberates dihydrobenzothiophene by interaction with the benzothiophene substrate [step (*f*)].

Besides accounting for the kinetic results, the mechanism proposed by Sánchez-Delgado comprises several steps which are commonly encountered in rhodium-catalysed olefin hydrogenation mechanisms. Also, unlike the Fish mechanism, the rhodium metal goes through the catalysis with the usual III ⟶ I ⟶ III reduction–oxidation cycle.

A kinetic study performed in 1,2-dichloroethane at 40 °C and ambient or subambient pressure of H_2 has recently been carried out on the hydrogenation of benzo[*b*]thiophene to dihydrobenzothiophene catalysed by $[Ir(cod)(PPh_3)_2]PF_6$.[25d]

Although displaying the same experimental rate law of the rhodium-catalysed reaction, $d[C_8H_8S]/dt = k_{cat}[Ir][H_2]$, the iridium-catalysed reaction shows a k_{cat} (25 °C) value of 3.9×10^2 $dm^3\ mol^{-1}\ s^{-1}$, which is surprisingly much higher than that observed for Rh. Consistently, the following activation parameters have been calculated: $E_a = 4.8$ kcal mol^{-1}, $\Delta H^‡ = 4.2$ kcal mol^{-1} and $\Delta S^‡ = -34.6$ e.u. Furthermore, the theoretical rate law fits with the experimental findings only by assuming the oxidative addition of H_2 to [Ir(σ-



Scheme 5 P = PPh_3

$SC_8H_8)(PPh_3)_2]^+$ [step (*e*) in the rhodium-catalysed mechanism shown in Scheme 5] as the rate-determining step.

The different kinetics observed for Rh and Ir have been related to the use of the different solvents used in the catalytic experiments: 2-methoxyethanol and 1,2-dichloroethane, respectively. In particular, it is suggested that the solvent affects the relative stability of some intermediates in the catalysis cycle without changing the mechanism in its fundamental steps.

Thiophene

A real example of catalytic hydrogenation of thiophene to tetrahydrothiophene has not been reported as yet. However, a case is known in which there is catalytic production of tetrahydrothiophene, although the reaction stops after two cycles only due to the formation of a bis(tetrahydrothiophene) metal complex which is stable under the experimental conditions.[25a]

The starting complex used in the hydrogenation of thiophene is the Ir^{III} dihydride $[IrH_2(\sigma\text{-}SC_4H_4)_2(PPh_3)_2]PF_6$, readily obtainable by treatment of $[Ir(cod)(PPh_3)_2]PF_6$ with H_2 in the presence of excess thiophene.[32] The dihydride complex reacts in 1,2-dichloroethane with thiophene at 80 °C under a steady stream of H_2 converting to the bis(tetrahydrothiophene) dihydride complex $[IrH_2(\sigma\text{-}SC_4H_8)_2(PPh_3)_2]PF_6$.

The mechanism for this hydrogenation of thiophene to tetrahydrothiophene has been elucidated by means of deuterium-labelling experiments as well as a variety of independent reactions with isolated compounds (Scheme 6).

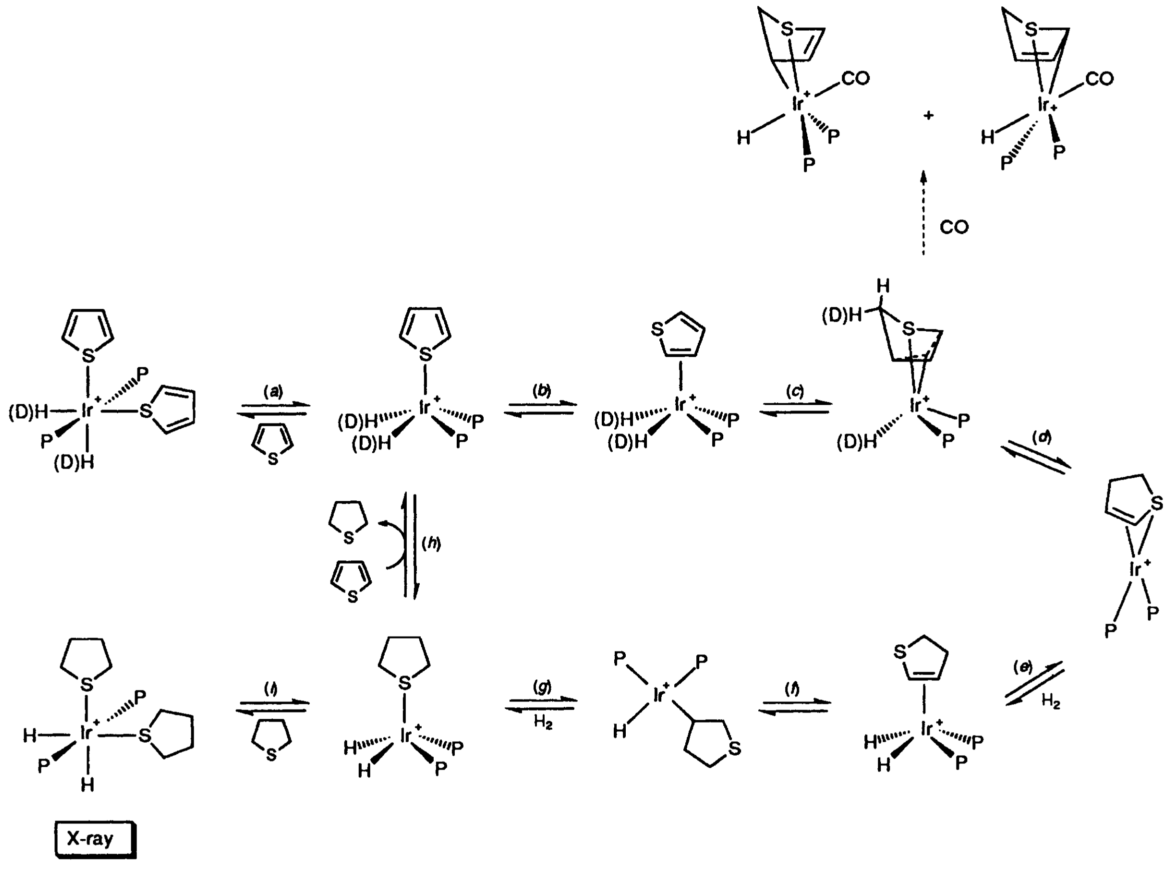
The first step of the proposed mechanism is the thermal elimination of one of the thiophene ligands from the bis(thiophene) precursor to give a 16-electron σ-S thiophene fragment. This is in equilibrium with the η^2-C^2,C^3 thiophene isomer [step (*b*)] which transforms into the thioallyl complex $[IrH(\eta^4\text{-}SC_4H_5)(PPh_3)_2]^+$ *via* stereospecific *endo* migration of one of the co-ordinated hydrides to the C^2 carbon atom [step (*c*)]. Subsequent migration of the remaining hydride to the C^3 carbon atom converts the thioallyl ligand to a 2,3-dihydrothiophene molecule which may use both the $C^4{=}C^5$ double bond and the sulfur atom [step (*d*)] for co-ordination.[33] The hydrogenation of this thiophene ligand to tetrahydrothiophene finally proceeds *via* the usual olefin hydrogenation mechanism [steps (*e*)–(*g*)]. Under the mild reaction conditions, the bis(tetrahydrothiophene) complex $[IrH_2(\sigma\text{-}SC_4H_8)_2(PPh_3)_2]^+$, which is formed by addition of tetrahydrothiophene [produced in step (*h*)] to the unsaturated fragment $[IrH_2(\sigma\text{-}SC_4H_8)(PPh_3)_2]^+$ is fully stable and practically blocks any further hydrogenation of thiophene.

Experimental evidence for the reaction sequence (*a*)–(*d*) has been provided by the isolation of the thioallyl complex and a study of its reactivity toward H_2, CO and syngas (CO–H_2). Furthermore, the use of pure samples of 2,3- and 2,5-dihydrothiophene in place of thiophene has unambiguously shown that only 2,3-dihydrothiophene is an intermediate in the homogeneous hydrogenation of thiophene to tetrahydrothiophene. This finding is consistent with previous proposals according to which the hydrogenation of thiophene to 2,3-dihydrothiophene precedes further hydrogenation and desulfurization (Scheme 7 summarizes two of the suggested mechanisms for the HDS of thiophene).[2,6]

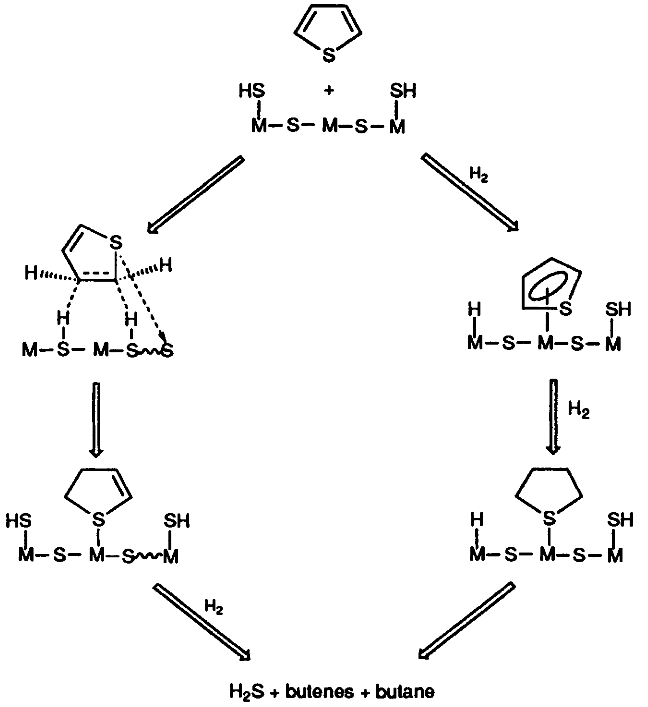
Catalytic Hydrogenolysis Reactions

For hydrogenolysis reactions we mean those metal-mediated transformations of thiophenes that result in the opening and hydrogenation of the substrates to give the corresponding unsaturated thiols, which eventually are reduced to the saturated derivatives (Scheme 8).

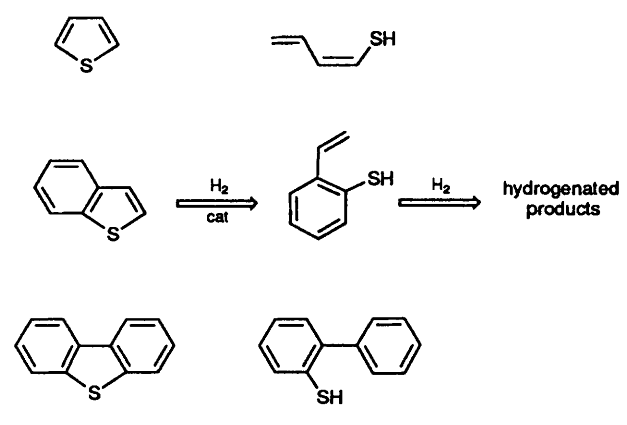
For the reasons forwarded in the case of the hydrogenation, the hydrogenolysis reactions of thiophenes are of great relevance in the HDS process as the aromatic thiols can be desulfurized by conventional heterogeneous catalysts under



Scheme 6 P = PPh₃



Scheme 7



Scheme 8

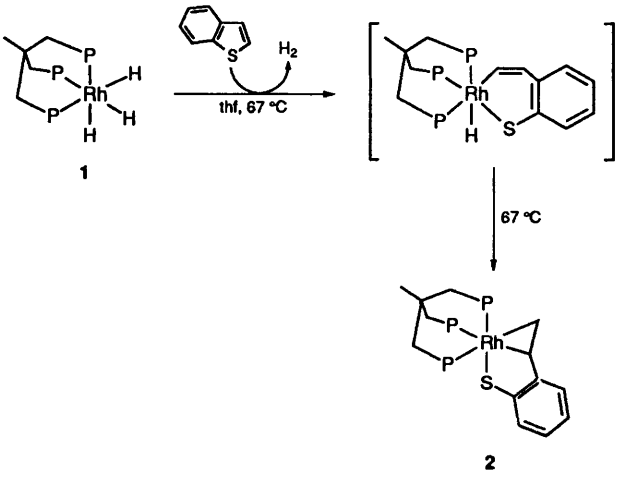
milder conditions than those required to desulfurize the thiophenes.[2]

Only hydrogenolysis reactions of benzo[*b*]thiophene and dibenzo[*b*,*d*]thiophene by soluble metal catalysts have been reported so far, whereas no example is known for thiophene. In our opinion, the lack of reports on the hydrogenolysis of thiophene is simply due to the difficulty in handling and detecting the evolved gaseous thiols. In fact, there is wide evidence in the literature that the energy barrier to the insertion of the metal into a C–S bond of thiophene is lower than those for opening benzo- and dibenzo-thiophene.[2,4,6] A similar trend of activity is shown by the heterogeneous HDS catalysts.[2,4]

Benzo[*b*]thiophene

The 16-electron fragment [RhH(triphos)], generated *in situ* by thermolysis of the trihydride [RhH$_3$(triphos)] **1** in refluxing thf, reacts with benzo[*b*]thiophene to give the 2-vinylthiophenolate complex [Rh{η^3-S(C$_6$H$_4$)CH=CH$_2$}(triphos)] **2** (Scheme 9).[7c]

The formation of **2** proceeds by regioselective insertion of rhodium into the C^2–S bond from benzo[*b*]thiophene, followed by intramolecular migration of the terminal hydride to the α-carbon atom of the metallathiacycle intermediate. The latter compound is not seen in the conversion of **1** to **2**, but an analogous complex can be intercepted by substituting the more kinetically inert iridium metal for rhodium.[7b,g]



Scheme 9

The 2-vinylthiophenolate complex **2** is an active catalyst precursor for the homogeneous opening and hydrogenation of benzothiopene into 2-ethylthiophenol with a mechanism that involves ring opening *prior* to hydrogenation.[25c]

At 160 °C and 30 atm H$_2$ in either thf or acetone, the conversion of benzothiophene to 2-ethylthiophenol occurs at an average rate of 13 mol (mol catalyst)$^{-1}$ h^{-1} in the first 2 h. The reaction is not fully selective as dihydrobenzothiophene is also formed (relative rate of 0.6) in an independent catalysis cycle.

Catalytic runs performed in different conditions show that the rate of formation of 2-ethylthiophenol increases significantly with the concentration of benzothiophene, while it is poorly affected by the H$_2$ pressure (the formation of 2-ethylthiophenol increases only by 5% in 16 h on going from 15 to 60 atm H$_2$). Below 15 atm H$_2$ and 100 °C, no appreciable transformation of benzothiophene is observed.

The catalytic system is truly homogeneous up to 180 °C as shown by the mercury test. Above 200 °C, appreciable decomposition of the catalyst occurs with formation of Rh metal particles which are responsible for the observed heterogeneous HDS of benzothiophene to ethylbenzene and H$_2$S.

High-pressure NMR spectroscopic studies in sapphire tubes show that, under catalytic conditions, all rhodium is incorporated into [RhH$_2${*o*-S(C$_6$H$_4$)Et}(triphos)] **3** and [{Rh[μ-*o*-S(C$_6$H$_4$)Et](η^2-triphos)}$_2$] **4** which are in equilibrium by H$_2$ elimination–addition (Fig. 1). Below 100 °C, ^{31}P-{^{1}H} NMR spectroscopy shows that only the dihydride complex **3** is present in solution. After quenching the catalytic reactions with a dinitrogen atmosphere, all rhodium is recovered as the bis(thiolate) complex [RhH{*o*-S(C$_6$H$_4$)Et}$_2$-(triphos)] **5**, which comes by the reaction of the dimer **4** with the 2-ethylthiophenol produced (Scheme 10).

Mechanistic interpretations for both the hydrogenolysis and the hydrogenation reactions of benzo[*b*]thiophene catalysed by the [RhH(triphos)] fragment have been proposed on the basis of the high-pressure NMR studies as well as several independent reactions with isolated compounds, some of which are summarized in Scheme 10.

The catalytic cycle (Scheme 11) begins with the stepwise hydrogenation of the 2-vinylthiophenolate ligand in the precursor to 2-ethylthiophenolate [steps (*a*) and (*b*)]. The unsaturated 16-electron fragment [Rh{*o*-S(C$_6$H$_4$)Et}(triphos)], which is formed by addition of H$_2$, either picks up further H$_2$ to form the dihydride **3** [step (*d*)] or dimerizes to **4** [step (*c*)], the latter path being favoured at high temperature and low H$_2$ pressure (see Fig. 1). The dihydride complex upon interaction with benzo[*b*]thiophene eliminates 2-ethylthiophenol and forms a σ-SC$_8$H$_6$ adduct [step (*e*)] (the dimer **4** is inactive towards benzo[*b*]thiophene in the catalytic reaction conditions). This reductive elimination of 2-ethylthiophenol is suggested to be the rate-determining step for the transformation of benzo[*b*]thiophene.

In the σ-S bonding mode, benzo[*b*]thiophene is activated in such a way that C–S insertion follows attack by the electron-rich Rh($^{\mathrm{I}}$) metal on the adjacent carbon atom (*via* electron donation into the C–S antibonding orbital).[6c] As a result of the C–S bond scission, the rhodabenzothiabenzene hydride intermediate is formed [step (*f*)], which regenerates the 2-vinylthiophenolate precursor **2** [step (*g*)] *via* hydride migration, thus closing the catalytic cycle.

The observed catalytic production of dihydrobenzothiophene is explained by taking into account a parallel catalysis cycle, similar to those described in the preceding section for the chemoselective hydrogenation of benzothiophene to dihydrobenzothiophene (which is stable under the actual reaction conditions).

The occurrence of the cycle (*i*)–(*k*) requires that the σ-S benzothiophene intermediate is in equilibrium with its η^2-2,3 isomer [step (*h*)], in which the C^2–C^3 double bond is activated for accepting a migrating hydrogen.[29] As a result, an alkyl intermediate [step (*i*)] is formed, which can oxidatively add H$_2$ and later eliminates dihydrobenzothiophene [steps (*j*)–(*k*)].

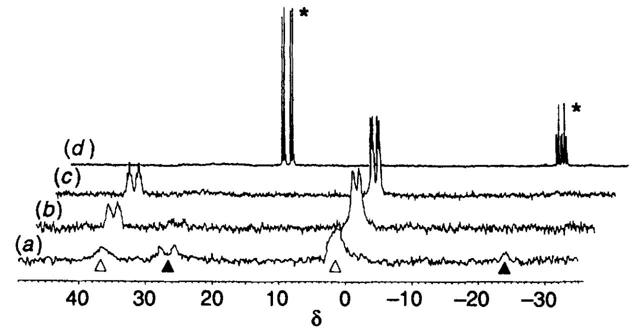


Fig. 1 ^{31}P-{^{1}H} high-pressure NMR study (sapphire tube, [^{2}H]$_8$thf, 81.01 MHz) of the catalytic hydrogenation of benzo[*b*]thiophene in the presence of complex **2** (30 atm H$_2$, substrate : catalyst ratio 100 : 1) after 4 h at 120 °C (*a*), after the NMR probe was sequentially cooled to 100 (*b*) and 80 °C (*c*), after all hydrogen was replaced by nitrogen (20 °C) (*d*); △ complex **3**, ▲ complex **4**, ★ complex **5**

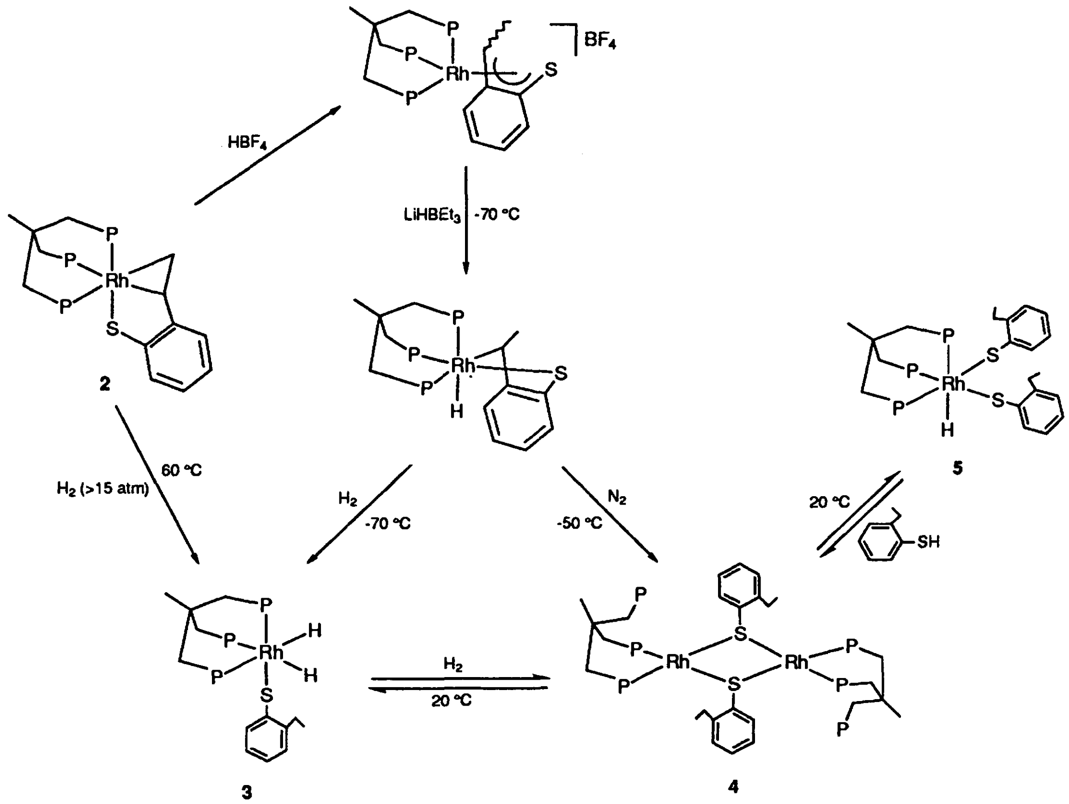
The observed prevalence of hydrogenolysis of benzo[*b*]thiophene to 2-ethylthiophenol over hydrogenation to dihydrobenzothiophene has been suggested as being driven by steric effects:[25c,29] although the Rh centre is sufficiently electron-rich to bind the C^2–C^3 double bond of benzothiophene, the large steric hindrance provided by the six phenyl substituents of triphos favours the σ-S co-ordination mode of benzothiophene, and ultimately controls the chemoselectivity of the reaction with H$_2$.

The most widely accepted mechanisms for HDS of benzothiophene over solid catalysts are shown in Scheme 12.[2,4,5] Path (*a*) begins with the selective hydrogenation to dihydrobenzothiophene prior to desulfurization, while path (*b*) involves initial C–S bond scission, followed by hydrogenation of the cleaved benzothiophene molecule.

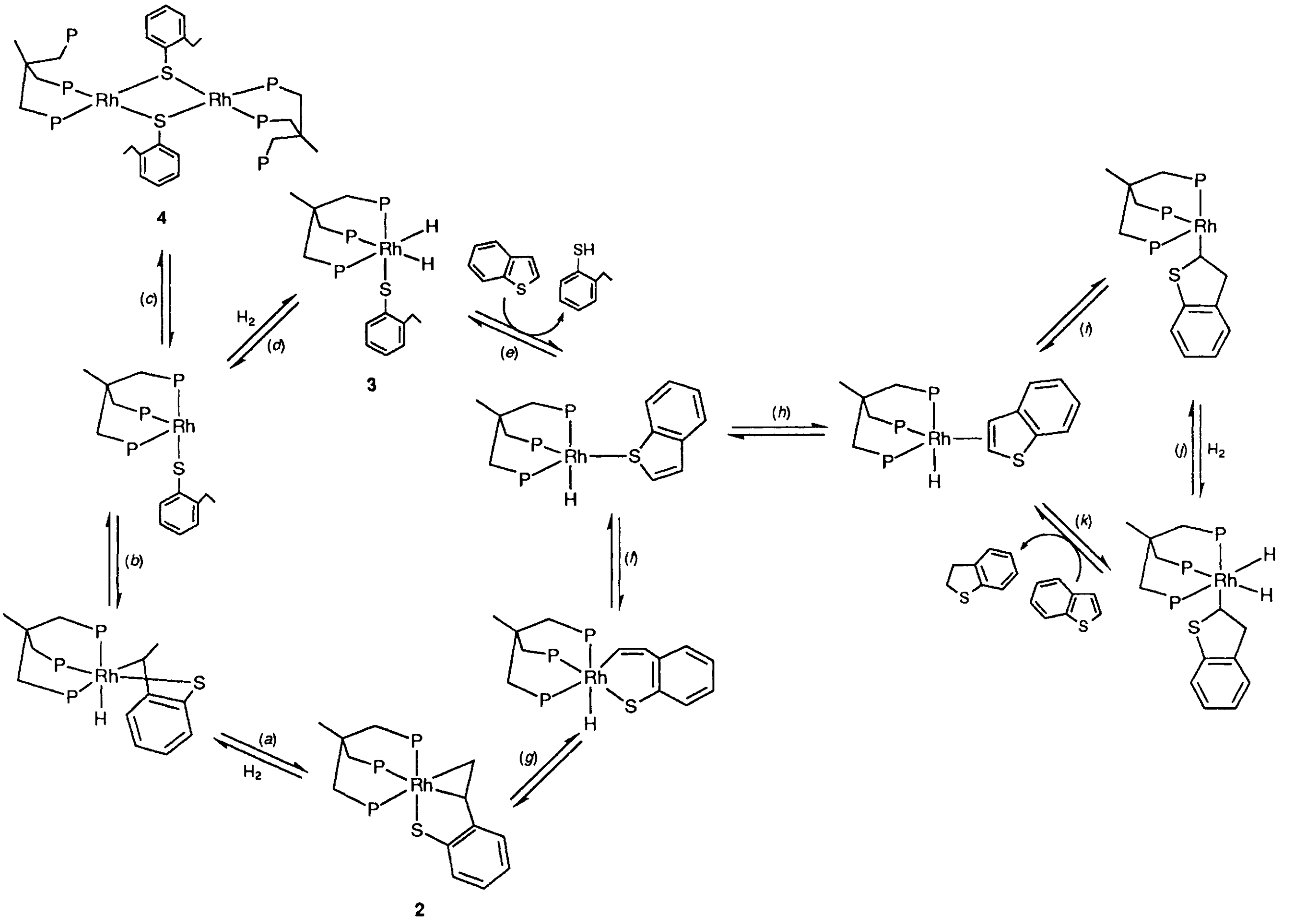
The results obtained with the homogeneous 'Rh(triphos)' system unambiguously show not only that the hydrogenolysis of benzothiophene to 2-ethylthiophenol occurs only after the substrate has been C–S inserted, but also that path (*b*) may be remodelled (dotted line in Scheme 12) so as to contain the hydrogenation of 2-vinyl- to 2-ethyl-thiophenol prior to the desulfurization step [which, in the case of the 'Rh(triphos)' system occurs as a heterogeneous process at temperatures ⩾200 °C].[25c]

Dibenzo[*b*,*d*]thiophene

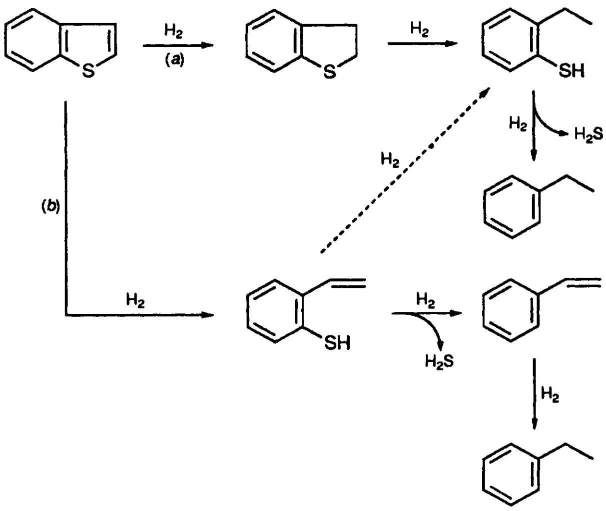
Thermolysis of the (ethyl)dihydride complex [IrH$_2$(Et)(triphos)] **6** in thf at 160 °C in the presence of an excess of dibenzo[*b*,*d*]thiophene results in the selective insertion of iridium into a C–S bond of the thiophenic molecule to give [IrH(η^2-*C*,*S*-C$_{12}$H$_8$S)(triphos)] **7**. At lower temperatures, kinetic C–H insertion compounds are also (< 160 °C) or exclusively (< 120 °C) produced (Scheme 13).[25b]



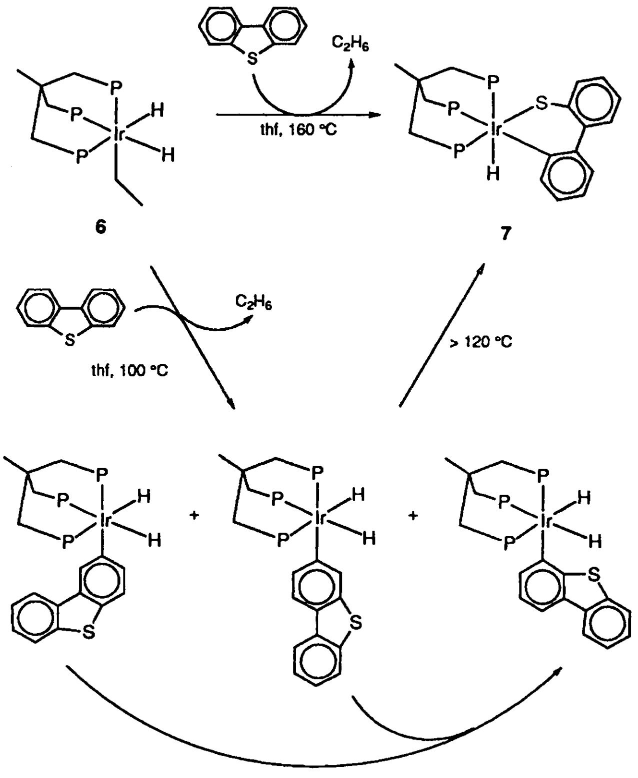
Scheme 10



Scheme 11



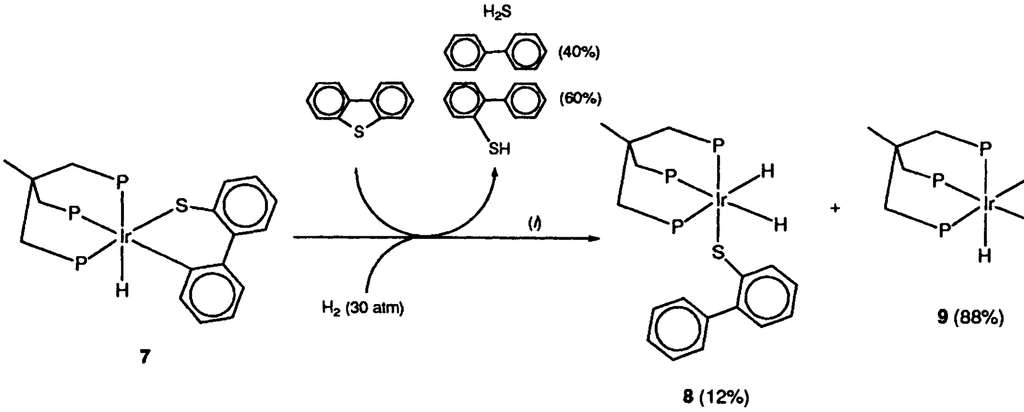
Scheme 12



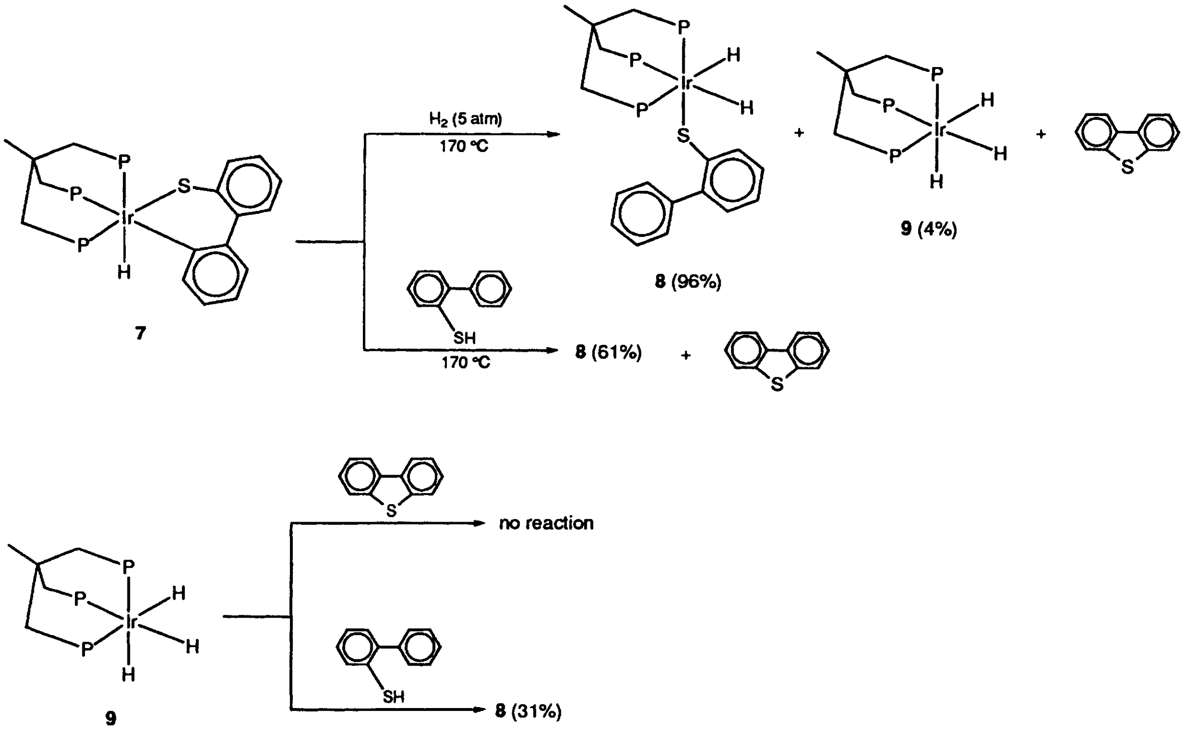
Scheme 13

The C–S insertion product **7** catalyses the homogeneous hydrogenation of dibenzo[*b*,*d*]thiophene (80-fold excess) in thf at 170 °C and 30 atm H_2 to give 2-phenylthiophenol, biphenyl and H_2S. The rate of transformation of dibenzothiophene is low as only 10 mol per mol of catalyst precursor are converted in 24 h to either open (rate 0.25) or desulfurized (rate 0.16) products (Scheme 14).

After the reaction is quenched, all iridium is incorporated into two complexes: the dihydride $[IrH_2(SC_{12}H_9)(triphos)]$ **8** and the trihydride $[IrH_3(triphos)]$ **9** in a 12:88 ratio. Based on this result as well as several independent reactions with isolated **8** and **9**, some of which are conveniently summarized in Schemes 15 and 16, a unique mechanism has been proposed to account for both the hydrogenolysis of dibenzothiophene to 2-



Scheme 14 (*i*) 170 °C, 24 h, 10 mol of dibenzo[*b*,*d*]thiophene per mol of 7



Scheme 15 Reaction conditions: thf, 4 h

phenylthiophenol and its desulfurization to biphenyl (Scheme 17).[25b]

For practical reasons, only the hydrogenolysis mechanism is discussed in this section, while the concomitant desulfurization mechanism will be described below.

The C–S insertion product 7 reacts with H_2 to give the 2-phenylthiophenolate dihydride complex 8. The reductive elimination of 2-phenylthiophenol from 8 is promoted by interaction with either free dibenzothiophene or H_2. In the former case, the precursor 7 is regenerated *via* the σ-$SC_{12}H_8$ intermediate {experimental evidence is provided for the existence of an equilibrium between [IrH(σ-$SC_{12}H_8$)(triphos)] and [IrH(η^2-*C*,*S*-$C_{12}H_8S$)(triphos)] in the experimental conditions}. On the other hand, 2-phenylthiophenol is formed also by action of H_2 on the dihydride 8 which is transformed into the trihydride 9. Although the latter complex does not react with dibenzothiophene, it can re-enter the catalytic cycle by reaction with the 2-phenythiophenol product (Schemes 15 and 17).

Besides the intrinsic kinetic sluggishness of iridium, the low turn-over frequency of the catalytic reaction is attributed to the slowness with which the trihydride 9 is converted to 8 by action of 2-phenylthiophenol, a reaction that, in fact, is disfavoured at the experimental high pressure of H_2.

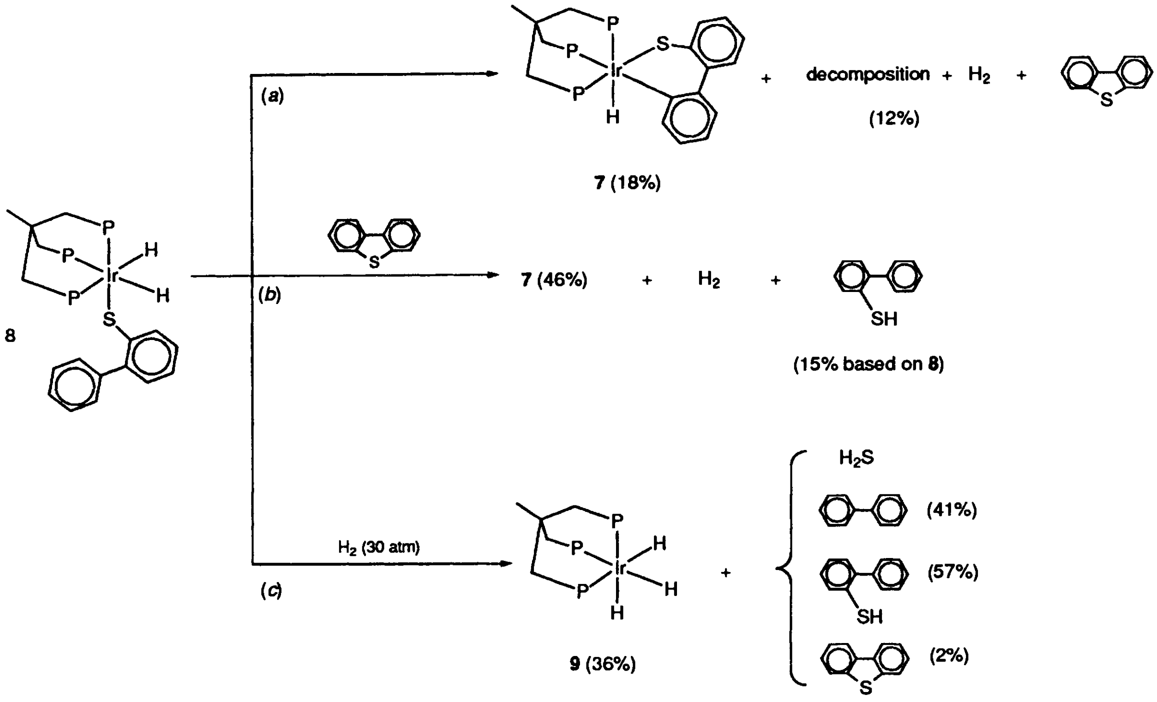
The principal mechanisms proposed for the HDS of dibenzothiophene over conventional heterogeneous catalysts are summarized in Scheme 18.

Path (*a*) involves the hydrogenation of one of the arene rings of dibenzothiophene to give, after consumption of 2 equivalents of H_2, tetrahydrodibenzothiophene, which, after C–S bond scission, is hydrogenated to 2-cyclohexylthiophenol. Path (*b*) is similar to one of the mechanisms suggested for HDS of benzothiophene (Scheme 12) as it primarily involves the opening and hydrogenation of the substrate to give 2-phenylthiophenol.

The limited number of benzo- and dibenzo-thiophene hydrogenolysis reactions catalysed by soluble metal complexes do not allow one to draw any general conclusions, particularly as regards the heterogeneous mechanism. Nevertheless the homogeneous modelling studies suggest that the HDS of dibenzothiophene (see also below) can proceed *via* ring opening to 2-phenylthiophenol prior to desulfurization and hydrogenation.

Catalytic Desulfurization Reactions

Under actual reactor conditions, the desulfurization of cleaved and hydrogenated thiophenes is not the step with the highest



Scheme 16 Reaction conditions: thf, 170 °C, 14 h

energy barrier.[2,4–6] In accord with the heterogeneous evidence, several soluble metal complexes have been found capable of desulfurizing activated thiophenic molecules under relatively mild conditions. However, with only one exception, all the reactions are stoichiometric in nature and generally require the use of a polynuclear metal system.

On the surface of a solid catalyst, the metal sites are held together by robust sulfur bridges that are not cleaved by H_2 under the drastic reaction conditions. Such a robustness is not shown by organometallic compounds that generally decompose when they are subjected to high H_2 pressures and temperatures as is the case of a catalytic desulfurization reaction.

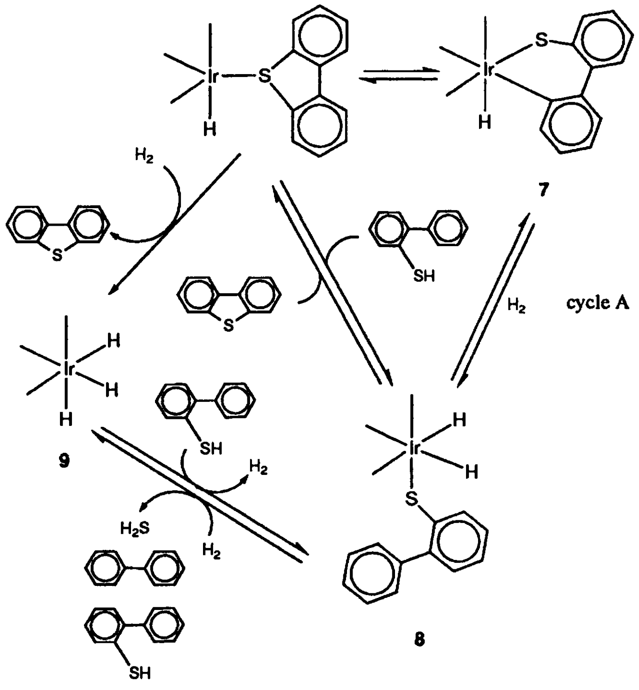
Dibenzo[*b*,*d*]thiophene

As shown in Scheme 17, the reaction of dibenzo[*b*,*d*]thiophene with H_2 (30 atm) in thf at 170 °C in the presence of the C–S insertion complex [IrH(η^2-*C*,*S*-$C_{12}H_8S$)(triphos)] **7** gives catalytic amounts of biphenyl and H_2S.[25b]

Like the hydrogenolysis to 2-phenylthiophenolate, the desulfurization reaction apparently proceeds *via* the intermediacy of the (thiolate)dihydride complex **8**. The key role of this compound in the desulfurization step is suggested by the reaction with H_2 (30 atm) at 170 °C that does result in the evolution of H_2S and biphenyl, and formation of the trihydride **9** [Scheme 16, path (*c*)].

The mechanism by which the C–S bond of the S-bonded thiolate is cleaved by H_2 is still undetermined. However, the relevant literature contains convincing evidence that the C–S bond cleavage in metal thiolates occurs *via* migration of a hydride to the sulfur-bound carbon atom.[2b,34] After the hydrocarbon is eliminated, the M–S moiety, in the presence of H_2, may form an M(SH)(H) species that, upon reductive elimination of H_2S, can regenerate the electron-rich metal species. A sequence of reaction steps of this type has recently been reported by Maitlis and co-workers (see below).[15]

Although not detected in the transformation of the thiolate **8** into the trihydride **9**, biphenyl and H_2S, a hydrosulfide complex of the formula [IrH_2(SH)(triphos)] **10**, independently synthesized, does react in thf with 30 atm of H_2 at 170 °C to form the trihydride **9** and H_2S. This finding suggests also that in the Ir-catalysed reaction, the desulfurization step proceeds *via* C–S bond cleavage by H_2 to give Ir–SH and biphenyl, followed by H_2S elimination (Scheme 19).

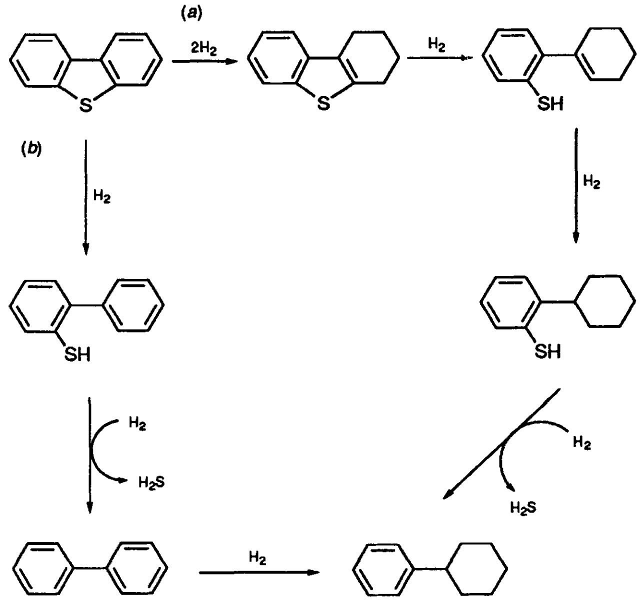


Scheme 17

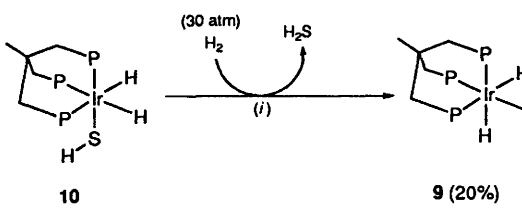
In conclusion, the iridium modelling study shows that H_2 can cleave the C–S bond of an unsaturated thiolate ligand derived from hydrogenolysis of dibenzo[*b*,*d*]thiophene and thus provides evidence that the desulfurization does not necessarily require the preliminary hydrogenation of one benzene ring of the dibenzothiophene (see Scheme 18).

Stoichiometric Desulfurization Reactions

The only example of HDS of a thiophenic molecule catalysed by a soluble metal complex is the one described above. However,



Scheme 18



Scheme 19 (*i*) thf, 170 °C, 14 h

given the importance of the desulfurization step in the HDS process, a number of examples are briefly described below in which the stoichiometric desulfurization of thiophenes occurs by action of metal complexes alone or aided by various reagents.

Polynuclear metal systems

The potential of the iron cluster $[Fe_3(CO)_{12}]$ as an activating agent toward thiophenic molecules has been widely explored by several research groups.[17–19]

The reaction of thiophene, 2-methyl-, 3-methyl- and 2,5-dimethyl-thiophene with $[Fe_3(CO)_{12}]$ in refluxing benzene has been found by Stone and co-workers,[18] Weiss and co-workers[19] and Rauchfuss and co-workers[17a] to proceed through the thiaferrole intermediate $[Fe_2(\mu\text{-}C_4HR_3S)(CO)_6]$ that cleanly transforms into the ferrole $[Fe_2(\mu\text{-}C_4HR_3)(CO)_6]$ with loss of the sulfur atom. The reactions leading to the thiaferroles are regiospecific: the iron invariably inserts into the less hindered C–S bond (Scheme 20).

The benzothiaferrole $[Fe_2(C_8H_6S)(CO)_6]$ has similarly been prepared by thermolysis in benzene of $[Fe_3(CO)_{12}]$ in the presence of benzo[*b*]thiophene.[17a] Unlike the thiophene derivatives, $[Fe_2(C_8H_6S)(CO)_6]$ is thermally stable in solution up to 180 °C under nitrogen. However, decomposition occurs under a hydrogen pressure (500 lbf in^{-2}) at 175 °C yielding ethylbenzene (hydrogenation, C–S hydrogenolysis) together with minor amounts of 2-ethylthiophenol (hydrogenation) and of bis(2-ethylphenyl) sulfide and bis(2-ethylphenyl) disulfide (Scheme 20).

No reaction is observed between $[Fe_3(CO)_{12}]$ and dibenzo[*b*,*d*]thiophene under the reaction conditions employed for thiophene and benzo[*b*]thiophene.

Examples of desulfurization of thiophenes promoted by $[Fe_3(CO)_{12}]$ have also been reported by Angelici and co-workers[20] and Rauchfuss and co-workers.[17b] Remarkably, the reaction described by Angelici proceeds *via* two distinct steps, the first of which involves the use of a metal (Ir) belonging to the family of the most active heterogeneous HDS promoters, to bring about the C–S bond scission of the thiophenic molecule. The following desulfurization of the C–S insertion product is then achieved by another metal (Fe), belonging to the family of the less active HDS promoters.

Although complicated by the formation of as many as eight different products, the reactions of the isomers $[Ir(Cp^*)(\eta^4\text{-}C_4H_2SMe_2\text{-}2,5)]$ and $[Ir(Cp^*)(C,S\text{-}C_4H_2SMe_2\text{-}2,5)]$ with the iron carbonyls $[Fe(CO)_5]$, $[Fe_2(CO)_9]$ and $[Fe_3(CO)_{12}]$ are intriguing.[20] Among the products obtained is $[Ir(Cp^*)\{C(Me)=CHCH=C(Me)\}\{\mu\text{-}SFe(CO)_4\}\{Fe(CO)_2\}]$ in which all the elements of 2,5-dimethylthiophene are retained, while both C–S bonds are cleaved (Scheme 21).

The structure of the Ir–Fe complex and the isomerization of the η^4-2,5-dimethylthiophene complex to the ring-opened complex (base-catalysed C–S bond cleavage, Scheme 21) constitute valid models for some steps in the heterogeneous HDS mechanisms which propose that the removal of sulfur from the thiophene ring occurs prior to its hydrogenation.

The η^4-thiophene complex $[Rh(Cp^*)(\eta^4\text{-}C_4Me_4S)]$ **11** reacts with $[Fe_3(CO)_{12}]$ in refluxing toluene to give the heterometallic ferrole $[Rh(Cp^*)\{(\eta^5\text{-}C_4Me_4Fe(CO)_3\}]$ **12** along with trace amounts of $[Rh(Cp^*)\{(\eta^4:\eta^1\text{-}C_4Me_4S)Fe(CO)_4\}]$ **13** which, however, plays a key role in the overall transformation (Scheme 22).[17b] Indeed, thermolysis of isolated **13** in refluxing toluene produces **12**, 'FeS', free C_4Me_4S and the cluster $[\{Rh(Cp^*)\}_2(\mu\text{-}CO)(\mu_3\text{-}S)\{Fe(CO)_3\}]$ **14** (Scheme 22). When the thermolysis reaction of **13** is carried out in the presence of added $[Fe_3(CO)_{12}]$, the Rh_2FeS cluster is formed only in traces. The fact that no reaction occurs between **14** and $[Fe_3(CO)_{12}]$ or C_4Me_4S in refluxing toluene has been interpreted by assuming that $[Fe_3(CO)_{12}]$ intercepts the intermediate species to **14**.

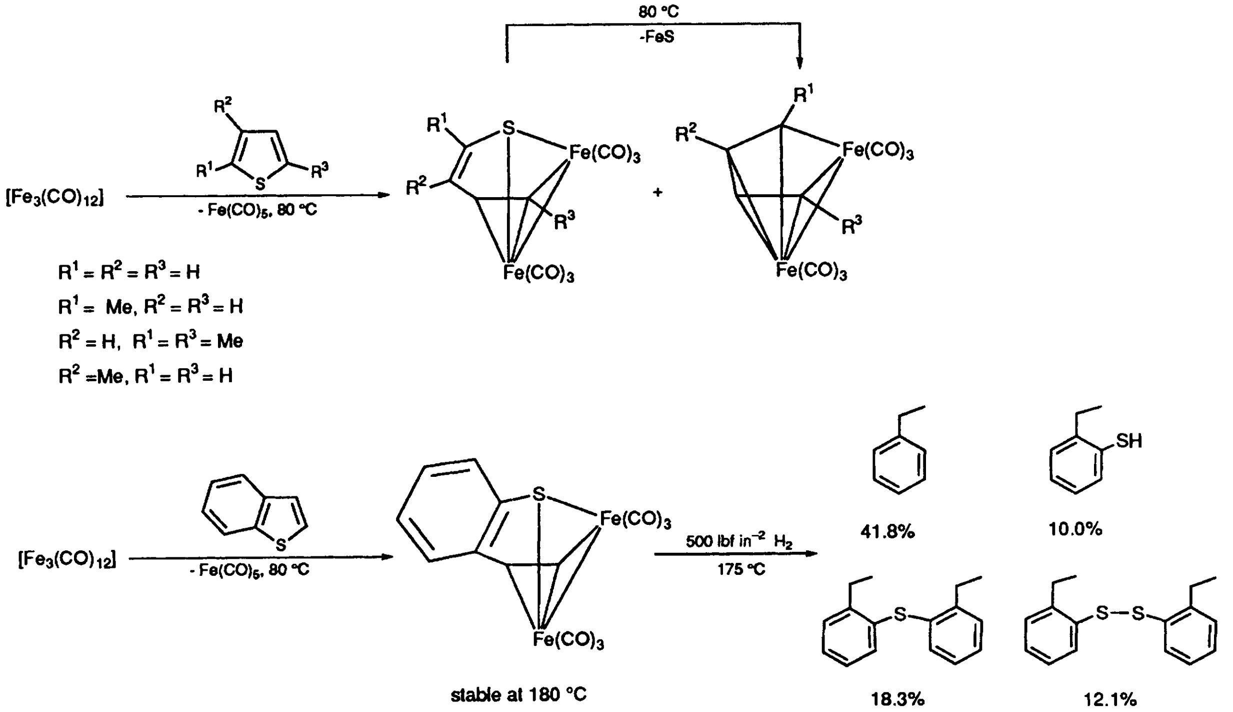
The desulfurization process reported in Scheme 22 has thrown some light onto the heterogeneous HDS mechanism. In fact, the desulfurized hydrocarbon fragment and the sulfur are separately bound to two distinct metal systems in such a way that the liberation of the butadiene and H_2S may be envisaged to occur by subsequent hydrogenation.

Like $[Fe_3(CO)_{12}]$, the analogous Ru cluster $[Ru_3(CO)_{12}]$ is capable of straightforwardly desulfurizing thiophenes.

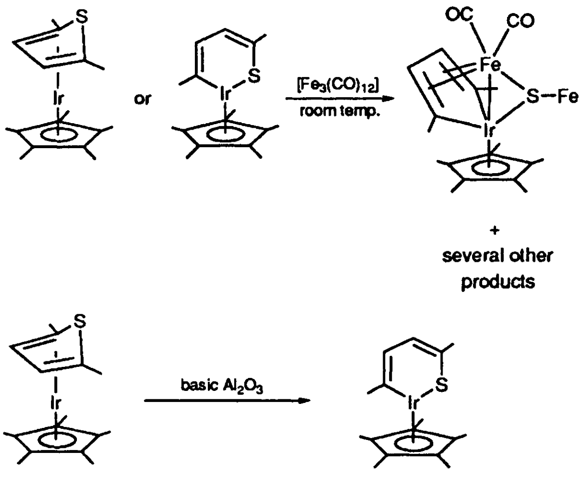
The reaction of $[Ru_3(CO)_{12}]$ and thiophene or 2-methylthiophene in thf at reflux temperature gives two metallacyclopentadiene complexes, $[Ru_2(\mu\text{-}C_4H_3R)(CO)_6]$ and $[Ru_4(\mu_3\text{-}S)(\mu\text{-}C_4H_3R)(CO)_{11}]$ (R = H or Me), by C–S bond cleavage (Scheme 23).[14a] In the latter compound, the inorganic (S) and the organic fragment (C_4H_3R) remain co-ordinated within the same organometallic framework. In addition to the C–S insertion products, C–H insertion products are also formed. The Ru cluster is also capable of cleaving both C–S bonds of benzo[*b*]thiophene to give ruthenaindene systems (compounds **15** and **16** in Scheme 23).[14b] Compound **17** is closely related to that obtained by Rauchfuss and co-workers[17a] in an analogous reaction with $[Fe_3(CO)_{12}]$ (Scheme 20).

The bimetallic cluster $[Mo_2(MeC_5H_4)_2Co_2S_3(CO)_4]$ reacts in neat thiophene at 150 °C under 15 atm H_2 to give almost quantitatively the cubane cluster $[Mo_2(MeC_5H_4)_2Co_2S_4(CO)_2]$ (Scheme 24).[16] The thiophene sulfur is incorporated into the cluster and the organic fragment is converted into saturated and unsaturated C_n ($n = 1$–4) hydrocarbons.

The desulfurization rates for methyl-substituted thiophenes are thiophene > 2-methyl- ≅ 3-methyl- > 2,5-dimethyl-thiophene. This trend parallels neither that over conventional heterogeneous catalysts (2,5-dimethyl > 3-methyl > 2-methyl > thiophene) nor that observed for heterogeneous catalysts prepared from $[Mo_2(MeC_5H_4)_2Co_2S_3(CO)_4]$ as a precursor (2-methyl > 3-methyl > 2,5-dimethyl > thiophene). Also, the proportion of cracking and hydrogenation products is greater



Scheme 20



Scheme 21

than that observed in heterogeneous HDS catalysis. Despite these results, the Curtis cluster is by far one of the best models for conventional heterogeneous 'CoMoS' phases.[35]

Jones and Chin[24] have recently reported that the cleavage of both C–S bonds of thiophene and the hydrogenation of the C_4 fragment to butadiene occur upon thermolysis of the polyhydride iridium dimer $[\{IrH_3(C_5Me_5)\}_2]$ in neat thiophene (Scheme 25). Most importantly, the butadiene molecule, bound to the dinuclear unit in an $\eta^2:\eta^2$ fashion, can be further hydrogenated by H_2 to butane.

Mononuclear metal systems

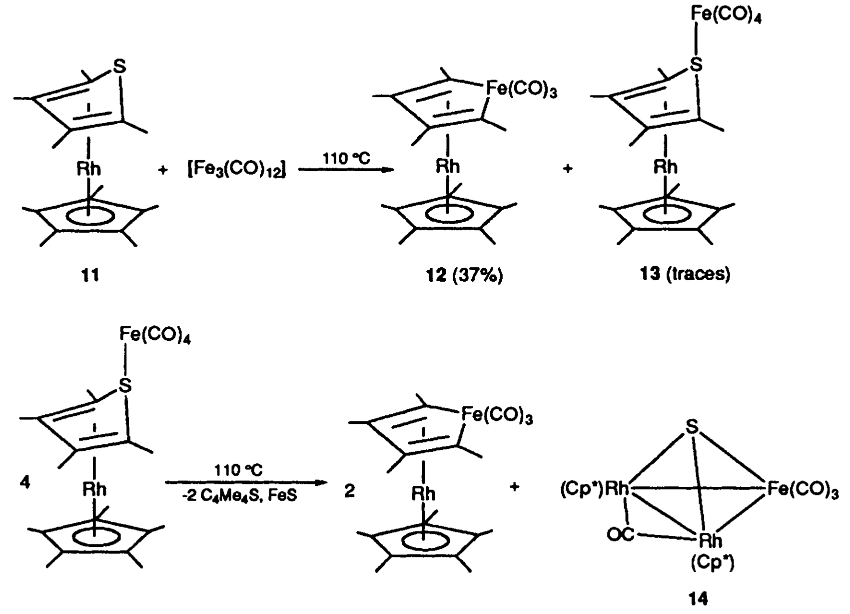
Although much less numerous than those assisted by polymetallic systems in either intramolecular or intermolecular fashion, a few examples of desulfurization reactions of thiophenes have also been observed by using mononuclear metal species. In general, however, an external source of hydrogen atoms is required to bring about the desulfurization step.

The butadienethiolate complex $[Ir(\eta^3\text{-}SCH{=}CH{-}CH{=}CH_2)(triphos)]$ is prepared by thermal reaction of thiophene in thf with either the dihydride $[IrH_2(Et)(triphos)]$ or the η^4-benzene complex $[Ir(\eta^4\text{-}C_6H_6)(triphos)]BPh_4$.[7a,g] In the latter case, the iridathiabenzene complex $[Ir(\eta^2\text{-}C,S\text{-}C_4H_4S)(triphos)]BPh_4$ is formed primarily, which converts to the butadienethiolate complex by hydride addition. Regioselective methylation of the thiolate sulfur atom with MeI gives $[Ir(\eta^3\text{-}MeSCH{=}CH{-}CH{=}CH_2)(triphos)]BPh_4$.[7a] Desulfurization of the butadienyl methylthioether ligand in the latter complex is achieved by BH_3·thf. Buta-1,3-diene is evolved, whereas the thiolate fragment remains co-ordinated to the metal (Scheme 26).[7a]

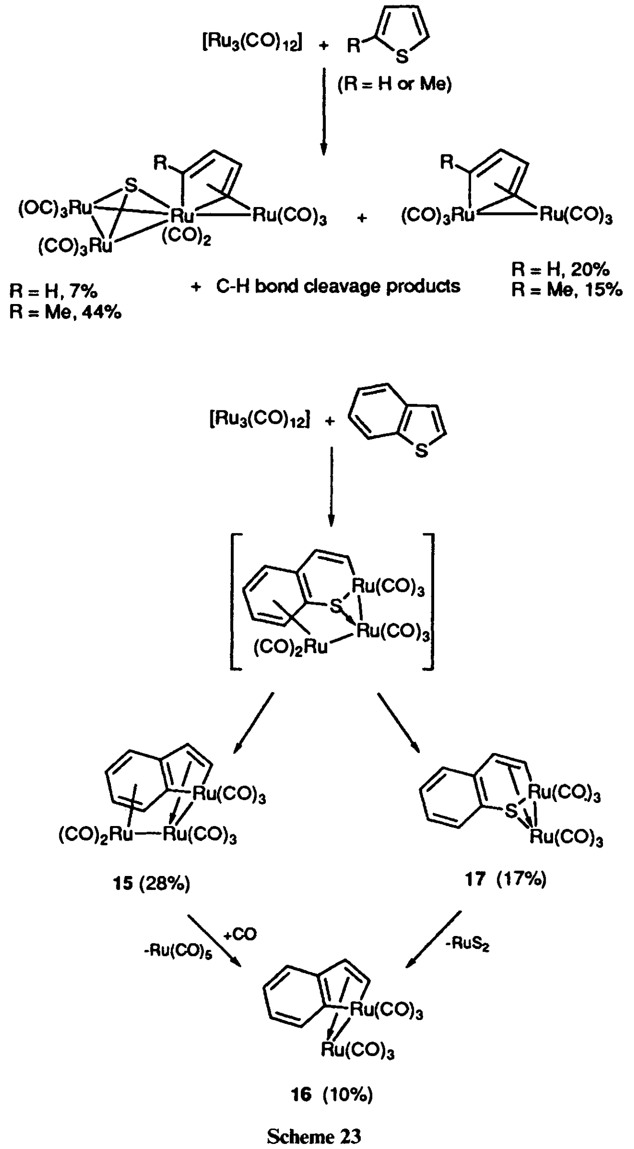
The thiaplatinacycles, $[Pt(SC_4H_4)(PEt_3)_2]$, $[Pt(SC_8H_6)(PEt_3)_2]$ and $[Pt(SC_{12}H_8)(PEt_3)_2]$ (Scheme 27), obtained by reaction of $[Pt(PEt_3)_3]$ with the appropriate thiophene, are hydrodesulfurized by hydride-releasing reagents (Et_3SiH, $NaBH_4$, Red-Al® or $LiAlH_4$) in refluxing toluene to give butadiene and butenes, styrene and ethylbenzene, or biphenyl, respectively.[15] The formation of the platinum thiol $[PtH(PEt_3)_2(SH)]$ invariably accompanies all of these hydrodesulfurization processes. A HDS mechanism occurring in two steps has been proposed: hydride-promoted cleavage of the Pt–C bond, followed by hydride-promoted cleavage of the remaining C–S bond.

The complex (2,2′-bipyridyl)(cycloocta-1,5-diene)nickel, [Ni(bipy)(cod)], is capable of desulfurizing dibenzo[*b*,*d*]thiophene to biphenyl in acid-hydrolysis conditions.[22a] A more powerful desulfurizing agent results from the interaction of equimolar amounts of the same nickel complex with $LiAlH_4$ in thf.[22b] The resulting Ni–Al adduct converts dibenzothiophene at 55 °C to biphenyl in greater than 90% yield (Scheme 28). On the basis of various considerations, a single-electron-transfer mechanism is proposed. The nickelocene–$LiAlH_4$ system is also an efficient desulfurizing agent for dibenzo[*b*,*d*]thiophene.[23]

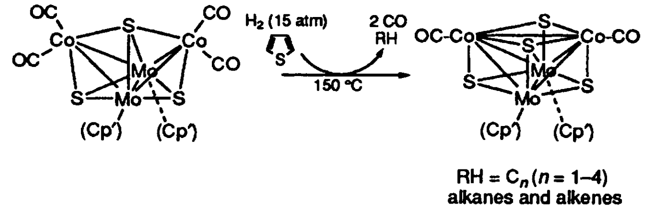
Finally, the bis(2-thienyl)zirconocene complex, prepared from $[ZrCl_2(Cp)_2]$ and (2-thienyl)lithium, decomposes in the temperature range 185–205 °C to give $[\{ZrS(Cp)_2\}_2]$ in *ca.* 80% yield (Scheme 29). The intermediacy of a ring-opened thiazirconacyclohexadiene species is proposed, whereas no information is given about the nature of the organic products released.[21]



Scheme 22



Scheme 23



Scheme 24 Cp′ = MeC_5H_4

The mechanisms of heterogeneous HDS of thiophene shown in Scheme 7 constitute only a fraction of the proposals that have been advanced on the basis of the reactor and surface studies.[2,4,5] Scheme 30 illustrates other possible pathways implicated in such mechanisms.

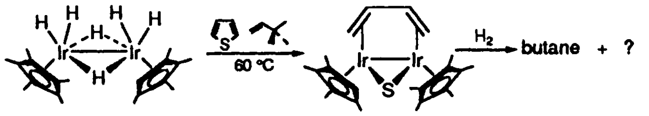
From a comparison of the homogeneous desulfurization reactions with the proposed HDS mechanisms, one may readily infer that several of the heterogeneous pathways have been substantiated by the homogeneous modelling studies. These, moreover, provide further insight into the potential role of the metal centres that neighbour the one at which chemisorption and activation of thiophene occurs. In fact, all of the desulfurization reactions reported in Schemes 20–25 do involve the concomitant action of two metals, one of which opens or activates the thiophene, while the other one promotes the extrusion of the sulfur atom. The latter step can occur either thermally or by treatment with H_2 (Schemes 20 and 24).

A mechanism that incorporates all the information obtained at the molecular level for the multimetallic HDS of thiophene is the one proposed by Angelici and co-workers (Scheme 31)[20] which may be extended also to both benzo[*b*]thiophene (see Schemes 20 and 23) and dibenzo[*b*,*d*]thiophene. For these substrates, in fact, the dehydrodesulfurization route shown in Scheme 30 is unlikely as it implies high-energy benzyne-type structures.

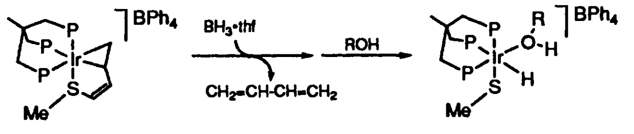
Among the few examples of stoichiometric desulfurization reactions of thiophenes promoted by mononuclear metal complexes, those involving the thiaplatinacycles (Scheme 27) are mechanistically relevant. In fact, the transformation of the cleaved thiophenes into H_2S and hydrocarbons occur by sequential addition of H^- and H^+ species that are present on the surface of conventional HDS catalysts, under the actual reaction conditions, in the form of hydryl (M–H) and sulfhydryl (S–H) moieties[30] (see Schemes 7 and 30).

Conclusion

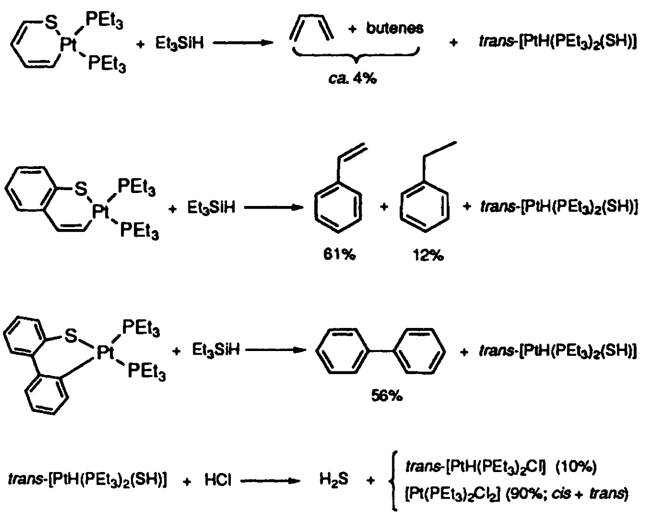
The data presented here define homogeneous metal catalysts as viable models for the first steps in the heterogeneously catalysed



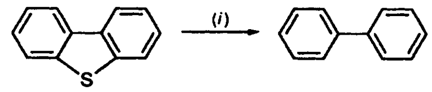
Scheme 25



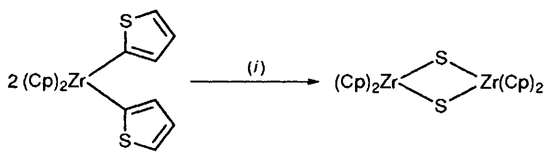
Scheme 26



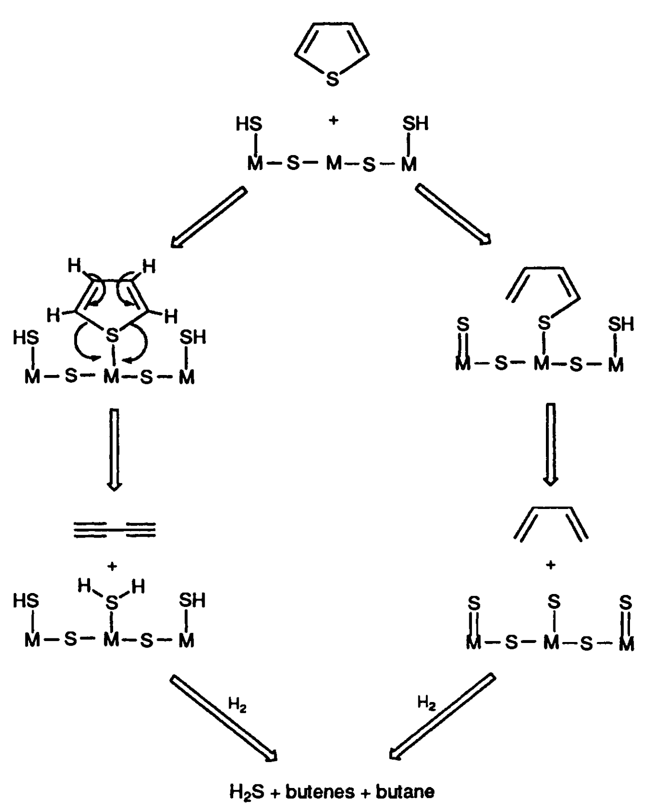
Scheme 27



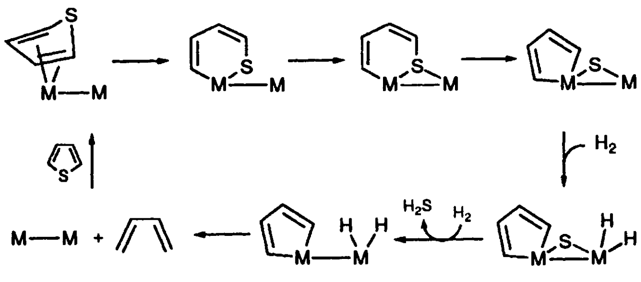
Scheme 28 (*i*) [Ni(bipy)(cod)], $LiAlH_4$, 90–95%



Scheme 29 (*i*) 185–205 °C, benzene or toluene



Scheme 30



Scheme 31

HDS reactions. In particular, it is shown that both the hydrogenation and the hydrogenolysis of thiophenic molecules can efficiently be accomplished by soluble metal catalysts through mechanisms which are not too dissimilar from those occurring over conventional heterogeneous catalysts. In contrast, the last step of the HDS process, namely the catalytic C–S bond cleavage, does not seem easily feasible in the homogeneous phase. Apparently such a step requires the use of cooperative multimetallic systems that may not be sufficiently stable under the experimental conditions needed to degrade the activated thiophene (generally in the form of either metallathiacycle or S-bound thiolate) into H_2S and hydrocarbon.

Although it is unrealistic to think of using a homogeneous catalyst in an HDS plant, molecular metal complexes may have a practical application for the purification of distillates in liquid-biphase systems. Indeed, liquid-biphase catalysis may be applied for the removal of the residual sulfur contaminants in distillates up to the limit of commercialisation of the gasoline. International regulations will soon require reducing the sulfur contents in fuels to less than 100 ppm, a limit which is beyond the range of activity of most of the commercially available HDS catalysts.

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