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An overview of modeling studies in HDS, HDN and HDO catalysis

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Abstract—Recent legislation directed at reducing sulfur levels in petroleum-based fuels has led to numerous studies of commercial hydrotreating, the process whereby sulfur, nitrogen, and oxygen are removed from organic compounds in petroleum feedstocks. The goal of this overview is to highlight organometallic and clean surface model studies that offer realistic ways of understanding details of hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrodeoxygenation (HDO) reactions as they occur on heterogeneous hydrotreating catalysts. © 1997 Elsevier Science Ltd

Keywords: hydrodesulfurization; hydrodenitrogenation; hydrodeoxygenation; thiophene; pyridine; furan.

This Symposium-in-Print is being published at a time when the petroleum industry around the world is seeking new ways to reduce sulfur levels in gasoline and other fuels. Currently, U.S. federal regulations require gasoline to contain no more than 0.1% sulfur (by weight), but this limit will be reduced to 0.04% by the year 2000; in California, only 0.003% sulfur will be permitted [1]. Similar reductions in sulfur levels are being imposed in European countries. As other parts of the world become more industrialized, the need to reduce sulfur levels will surely increase.

Hydrodesulfurization (HDS) is the process whereby sulfur is removed from organosulfur compounds that are present in petroleum distillates and other feedstocks by treatment with hydrogen gas (up to 200 atm pressure) at temperatures of 300–450°C. The reaction conditions depend, in part, on the sulfur contents of the feedstocks which typically range from 0.2 to 4%. The most commonly-used catalyst is a combination of cobalt and molybdenum supported on Al_2O_3. The Co and Mo exist primarily as Co_9S_8 and MoS_2 [1,2]. Under HDS conditions, removal of nitrogen and oxygen from their organic compounds in petroleum also occurs. These processes are known as hydrodenitrogenation (HDN) and hydrodeoxygenation (HDO) [3] and are represented, along with HDS, by eqs (1), (2) and (3).

$$C_aH_bS + c\,H_2 \longrightarrow H_2S + C_aH_d \quad (1)$$

$$C_aH_bN + c\,H_2 \longrightarrow NH_3 + C_aH_d \quad (2)$$

$$C_aH_bO + c\,H_2 \longrightarrow H_2O + C_aH_d \quad (3)$$

This treatment of petroleum feedstocks with hydrogen gas is known as hydrotreating and is performed on a very large scale commercially: 26 million barrels of feedstocks per day worldwide and 8.2 million barrels per day in the U.S.A. in 1995 [4]. In addition to HDS, HDN and HDO, hydrogenation of unsaturated hydrocarbons also occurs; these latter reactions are usually undesirable because of the high cost of H_2.

The reasons for removing sulfur from petroleum feedstocks are not only to reduce the amount of sulfur

oxides released into the atmosphere during the combustion of hydrocarbon fuels, but also to reduce sulfur poisoning of precious metal-based reforming catalysts that are used in producing high octane gasoline. Nitrogen removal is performed in order to reduce nitrogen oxide emissions from burning fuels and to prevent basic amine poisoning of zeolitic cracking catalysts which are used to generate gasoline-sized molecules from larger hydrocarbons. Typically, nitrogen levels in crude oils are only 0.1–0.9% by weight. The $CoMo/Al_2O_3$ catalyst which is highly effective for HDS is less active for HDN. When nitrogen removal is especially important, a $NiMo/Al_2O_3$ catalyst is preferred. Oxygen levels in crude oils are usually low ($<0.1\%$), and while HDO occurs under hydrotreating conditions, oxygen removal is generally not a goal of this process.

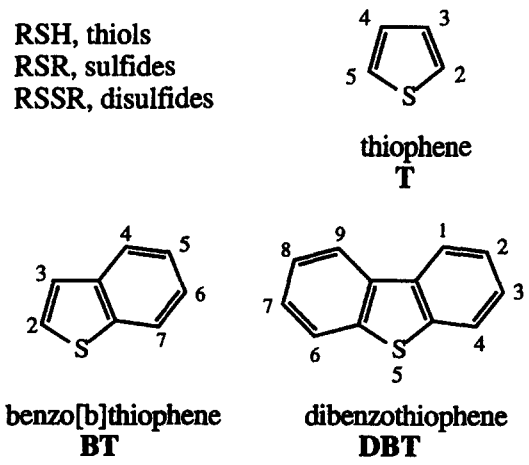
The model studies described in this Symposium-in-Print attempt to understand how adsorption and reaction of molecules occur under the strenuous process conditions used for HDS, HDN and HDO. Whether the models are organometallic complexes or molecules on single metal crystals under ultra high vacuum, they represent situations that are very different from those used in hydrotreating. For this reason, results of model studies may or may not be relevant to reactions performed under catalytic conditions; however, they do provide realistic examples of how reactants *might* adsorb and react. And they have also opened up many new ways of thinking about how these processes might occur on a catalyst—ways that had not been previously imagined. Model studies also help us to distinguish between "reasonable" and "less reasonable" mechanisms that were proposed in the past. While these studies suggest how hydrotreating reactions *might* occur, it is necessary to design experiments that will test the validity of each model. Such experiments, a few of which have been reported, begin to bridge the rather sizeable gap between the modeling and heterogeneous catalysis engineering communities.

In this lead-off article, I give brief overviews of HDS, HDN and HDO in an effort to highlight some of the reported modeling studies; the coverage is not intended to be comprehensive. Much more has been done on HDS than HDN, while HDO has been investigated relatively little.

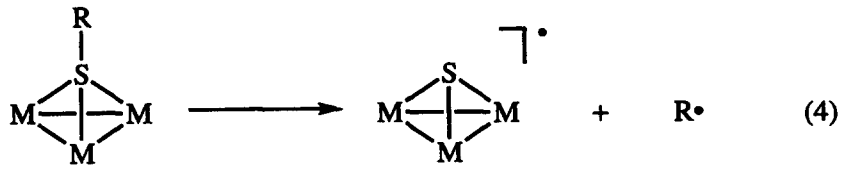
HYDRODESULFURIZATION (HDS)

The types of organosulfur compounds present in petroleum feedstocks are shown in Table 1 [5–8]. The alkyl and aryl thiols (RSH), thioethers (RSR′) and disulfides (RSSR′) undergo HDS [eq. (1)] under the mildest conditions and are therefore desulfurized more readily than the aromatically stabilized thiophene [9,10]. It is the thiophenes that require the strenuous conditions employed in hydrotreating. While the thiophenes, benzo[b]thiophenes and most dibenzothiophenes are desulfurized under current process conditions, future regulations will also require desulfurization of relatively unreactive dibenzothiophenes [11,12] that are substituted in the 4,6-positions such as 4,6-dimethyldibenzothiophene (4,6-Me_2DBT). These sterically hindered dibenzothiophenes represent a major challenge for researchers in HDS. For each of the different types of organosulfur compounds in Table 1, HDS reaction products, intermediates, thermodynamics and kinetics have been summarized by Girgis and Gates [13].

Table 1. Types of organosulfur compounds in petroleum

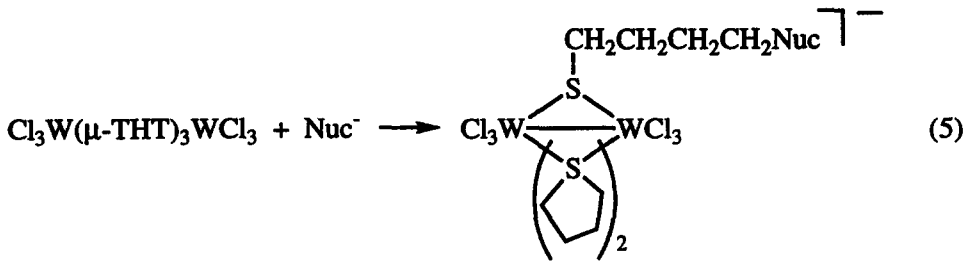


Model studies of all of the classes (Table 1) of organosulfur compounds have been reported. Organic chemists have used transition metal complexes, including metal carbonyls [14], extensively as stoichiometric reagents for the desulfurization of thiols and thioethers. In an effort to understand how metal complexes promote C—S cleavage in thiols, Curtis [15] showed that the C—S bond of the thiolate (RS^-, R = aryl, *t*-Bu) ligand in the cluster complex $Cp'_2Mo_2Co_2S_3(CO)_3(SR)^-$ is cleaved homolytically when the cluster is refluxed in acetonitrile. This cleavage is presumably promoted by the formation of a stable μ_3-sulfide complex [eq. (4)],



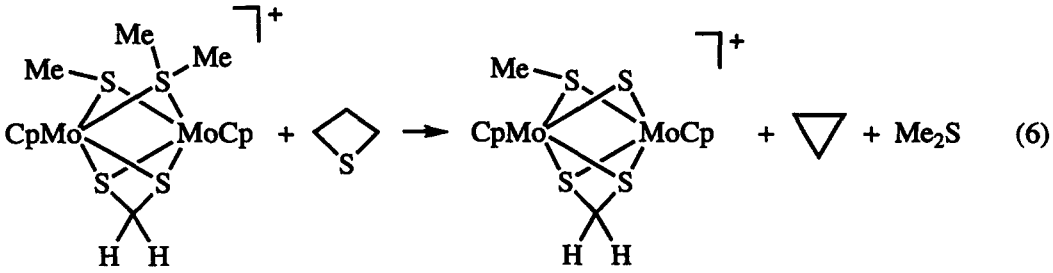
(4)

which provides the driving force for the reaction. Heterolytic C—S bond cleavage of the thioether tetrahydrothiophene (THT) ligand has been observed [16] in reactions of $Cl_3W(\mu\text{-THT})_3WCl_3$, which contains three sulfur-bridging THT ligands, with nucleophiles (Nuc^-) such as SR^-, SeR^-, Cl^-, Br^- and H^- [eq. (5)].



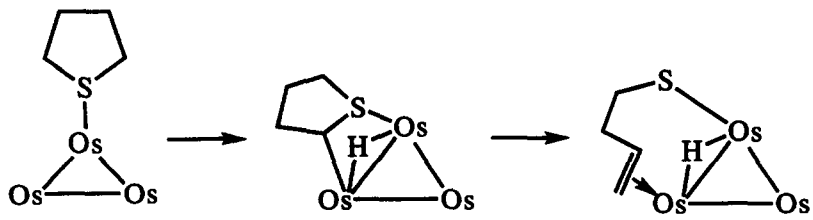
(5)

In this case, the electron-withdrawing W(III) centers presumably make the α-CH_2 of the THT susceptible to nucleophilic attack. Thiols such as CH_3SH undergo rapid C—S cleavage on single crystal metal surfaces under UHV conditions to give hydrocarbons and a surface sulfide [17,18]. Cyclic thioethers such as thietane (C_3H_6S) and tetrahydrothiophene (THT, C_4H_8S) undergo initial C—S bond cleavage on Mo(110) to give adsorbed thiolates (propanethiolate or butanethiolate), which then decompose to give the corresponding alkane or alkene and the surface sulfide [17,18]. As in its reaction on Mo(110), thietane reacts with a dinuclear molybdenum complex to give cyclopropane and the sulfide complex [eq. (6)] [19]. An organometallic model for



(6)

THT ring-opening on Mo(110) is provided by the transformations in eq. (7) that occur on an $Os_3(CO)_{10}$

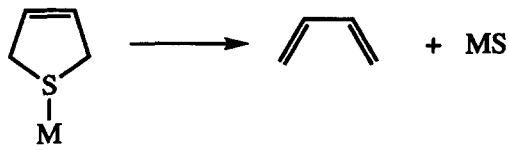


(7)

cluster core [20]. These are typical examples of organometallic model reactions that provide possible detailed mechanisms for reactions of cyclic thioethers that occur on metal surfaces.

The unsaturated thioether 2,5-dihydrothiophene (2,5-DHT), which we have proposed [21,22] as an intermediate in a mechanism for the HDS of thiophene, decomposes on Mo(110) to give butadiene selectively and

the surface sulfide [eq. (8)] [18,23]. Butadiene is also the major product of 2,5-DHT hydrodesulfurization over



(8)

a 5% Re/Al_2O_3 catalyst at 300°C [22(a)]. The 2,5-DHT ligand, when coordinated to a metal through the sulfur, in the complexes L_xM(2,5-DHT), where $L_xM = W(CO)_5$, $Fe(CO)_4$ or $Re_2(CO)_9$, also decomposes [eq. (8)] by releasing butadiene [24]. Presumably, sulfur-coordination of 2,5-DHT to a metal center, whether on Mo(110), on an HDS catalyst or in a complex, promotes butadiene evolution.

Thiophene is the organosulfur compound that has been most extensively investigated by organometallic modeling. Because of the central role of molybdenum in commercial HDS catalysis, one would expect the literature to be filled with molybdenum-thiophene complexes. Yet none has been reported despite numerous efforts by several research groups. A partial exception to this statement is *fac*-$Mo(CO)_3$[2,5-$(Ph_2PCH_2CH_2)_2C_4H_2S$] in which the thiophene portion of the tridentate ligand 2,5-$(Ph_2PCH_2CH_2)_2C_4H_2S$ is η^1(S)-coordinated to the molybdenum [25]; the coordinating PPh_2 groups presumably provide the necessary driving force for sulfur coordination of the thiophene group. It is not obvious, however, why simple thiophene complexes are not stable; it might be noted that several other metals, e.g., Ru, Os, Rh, Ir and Re, have higher HDS activities than Mo [26,27], and thiophene complexes are known for all of these metals [28].

In its complexes, thiophene coordinates in the several different modes shown in Fig. 1; reviews of the many complexes that contain thiophene ligands have been published [28–30]. In principle, thiophene could adsorb to metal sites on HDS catalysts in any of these ways. Raman, infrared emission (IRE), and inelastic tunneling (IET) spectroscopic studies by Diemann, Weber, and Müller show that thiophene adsorbs to MoS_2/Al_2O_3 only when the MoS_2 is reduced by H_2 [31]. Based on vibrational data and MO calculations, the authors propose that thiophene coordinates through its sulfur to a Mo^{II} site. It would be useful to compare these spectroscopic results for thiophene on reduced MoS_2/Al_2O_3 with analogous data for thiophene complexes exhibiting the coordination modes in Fig. 1. Spectroscopic studies of single metal crystals indicate that thiophene may adsorb on Pt(111) either by coordinating through its sulfur atom but tilted with respect to the surface or by η^5-bonding with the thiophene molecular plane oriented parallel to the surface [32]. In general, thiophene is very reactive

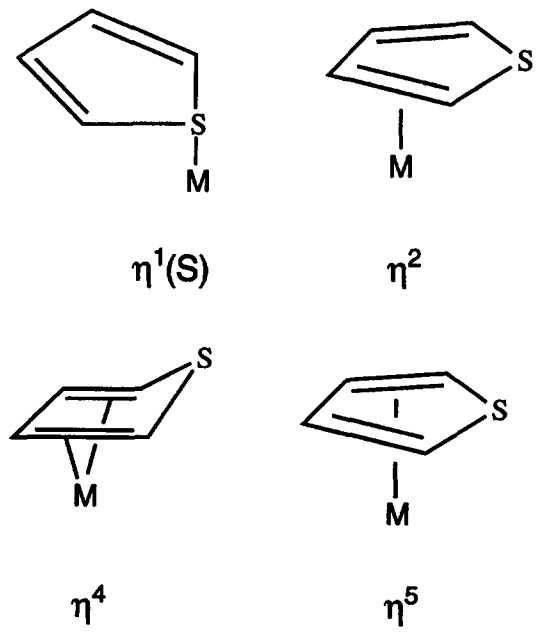
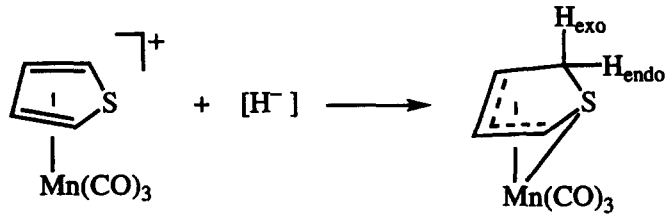


Fig. 1. Known modes of thiophene coordination in transition metal complexes.

on single crystal metal surfaces and undergoes non-selective decomposition to carbon and other products [17,18,33]. On the other hand, several studies [34] show that thiophene is *formed* from acetylene and sulfur on Pd(111) surfaces.

In all structurally characterized organometallic complexes containing η^1(S)-coordinated thiophene, the metal does not lie in the plane of the thiophene; the sulfur may be described as approximately sp^3 hybridized [28–30]. There are no X-ray-determined structures of η^2-thiophenes, although the $Os(NH_3)_5(2,3\text{-}\eta^2\text{-Thi})^{2+}$ complexes, where Thi is thiophene or a substituted thiophene, are well-characterized spectroscopically [35]. Selenophene, the Se analog of thiophene, is 2,3-η^2 coordinated in $Cp'Re(CO)_2(2,3\text{-}\eta^2\text{-Sel})$ [36]. And benzo[b-]thiophene (BT) forms complexes $Cp'Re(CO)_2(BT)$ that exist as equilibrium mixtures of isomers exhibiting the 2,3-η^2- and η^1(S)-coordination modes [37]. Although well-refined X-ray structures were not obtained for either $Cp'Re(CO)_2(2,3\text{-}\eta^2\text{-Sel})$ or $Cp'Re(CO)_2(2,3\text{-}\eta^2\text{-BT})$, structures of some of their derivatives have been reported [36,38,39]. Several structural determinations of η^4- and η^5-thiophene complexes have been reported [28–30]. Molecular orbital calculations of thiophene bonding to metal centers in organometallic complexes [40] and on catalyst surfaces [41–43] have been used to estimate the most favorable bonding modes and types of reactivity expected from adsorbed thiophene.

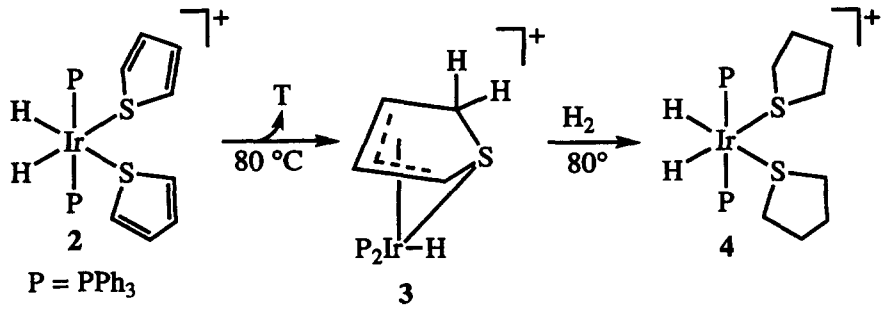
While thiophene in its complexes undergoes a variety of reactions, I discuss below only those reactions that seem most relevant to catalytic HDS; they often lead to C—S bond cleavage. Initially, reactions of thiophene in relatively positive metal complexes are discussed; in this environment thiophene is often attacked by nucleophiles. Next, reactions of relatively electron-rich complexes will be examined. Nucleophilic addition has been reported only for η^5-thiophene complexes. The metal presumably withdraws electron-density from the thiophene making it susceptible to attack by nucleophiles. The cationic $Mn(CO)_3(\eta^5\text{-T})^+$ reacts [eq. (9)] with



(9)

1

hydride sources ($HFe(CO)_4^-$, $HW(CO)_5^-$ or BH_4^-), as well as other nucleophiles (CN^- and PBu_3^n), to give the allyl sulfide product **1** [44,45]. A related allyl sulfide $ReH_2(PPh_3)_2(\eta^4\text{-}C_4H_5S)$ was prepared by reaction of $ReH_7(PPh_3)_2$ with thiophene in the presence of the hydrogen acceptor *t*-BuCH = CH_2 [46]. This reaction presumably involves transfer of a hydride ligand to a coordinated thiophene. This type of mechanistic step is supported by the conversion of **2** to **3** in eq. (10) [47]. The allyl sulfide ligand in **3** may be subsequently



(10)

2

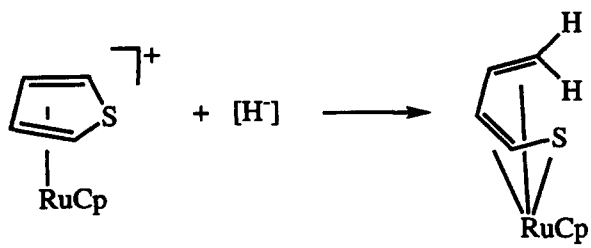
P = PPh_3

3

4

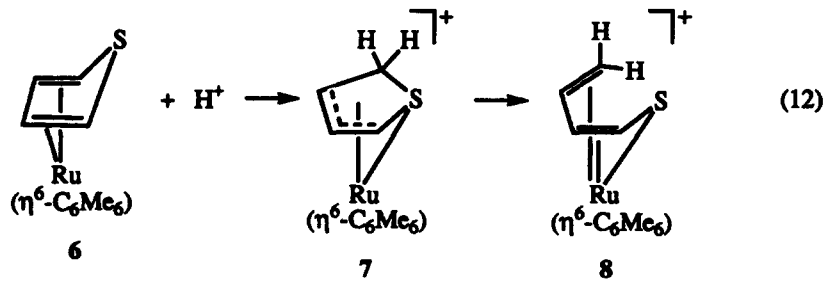
converted to tetrahydrothiophene in **4** upon reaction with H_2. Complex **2** also reacts with excess thiophene under H_2 (1 atm) to give **4**.

The reaction [eq. (11)] of hydrides (AlH_4^-, $H_2Al(OCH_2CH_2OMe)_2^-$ or $HBEt_3^-$) with the η^5-T ligand in



(11)

$CpRu(\eta^5\text{-T})^+$ not only results in addition of H^- to the C(2) position but also causes cleavage of the C—S bond to give a butadiene thiolate ligand (**5**) [48]. It is not obvious why C—S cleavage occurs in reaction (11) but not in (9). Rauchfuss [49,50] showed that a butadiene thiolate ligand may also be generated by electrophilic addition [eq. (12)] of H^+ to the C(2) carbon of an electron-rich η^4-thiophene complex to give initially an allyl

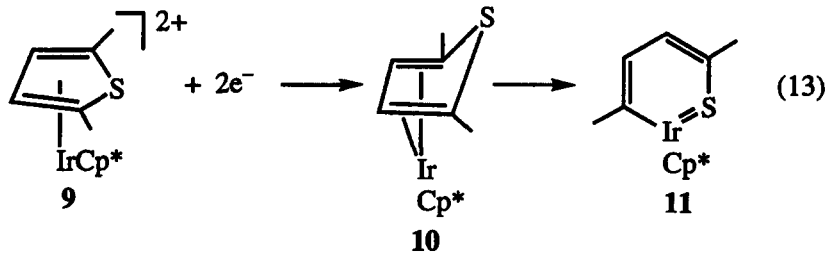


(12)

sulfide complex (**7**) which subsequently undergoes ring-opening to the butadiene thiolate product **8**.

The C—S cleavage reactions in eqs (11) and (12) require η^5 or η^4 thiophene coordination to a metal. Since BT and DBT do not coordinate in this manner [30], these benzothiophenes do not undergo reactions that lead to C—S cleavage by processes analogous to those in eqs (11) and (12). A common mode of BT and DBT coordination is η^6 through the benzo-rings. However, there is no evidence that this type of coordination promotes reactions that result in C—S bond cleavage [51,52]. The 2,3-η^2-coordinated form [37] of BT is presumably an intermediate in catalytic hydrogenation reactions [53,54] that give 2,3-dihydrobenzothiophene, an intermediate in the HDS of BT [37]. Sulfur-coordinated BT and DBT complexes do not undergo C—S cleavage reactions, but they may be precursors to intermediates that lead to insertion of a metal into a C—S bond as discussed below.

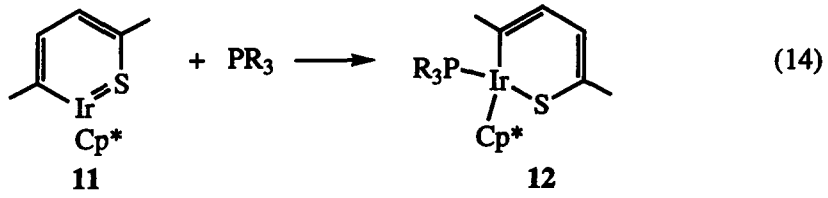
The η^5-thiophene ligands in $Cp^*Ir(\eta^5\text{-Thi})^{2+}$ do not undergo nucleophilic attack by H^- donors, as in eqs (9) and (11). Instead, $H_2Al(OCH_2CH_2OMe)_2^-$, as well as the reducing agent Cp_2Co, simply donates two electrons to give [eq. (13)] the η^4-thiophene complex **10** [55]. In the presence of bases or during ultraviolet photolysis,



(13)

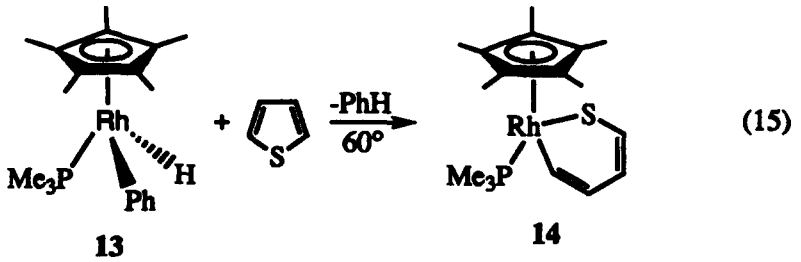
10 isomerizes to **11** with the insertion of the Ir into a C—S bond of the thiophene ligand. Thus, the overall effect of reducing complex **9** is cleavage of a thiophene C—S bond. Oxidation of **11** with two equivalents of Cp_2Fe^+ gives **9** quantitatively, which results in making a C—S bond. Thus, simple reduction and oxidation leads to C—S bond breaking or making. The analogous $Cp^*Rh(\eta^5\text{-}Me_4T)^{2+}$, where Me_4T is tetramethylthiophene, is also reduced by Cp_2Co to give $Cp^*Rh(\eta^4\text{-}Me_4T)$ [56], which is not reported to rearrange to the ring-opened analog of **11**. Reduction of $(\eta^6\text{-}C_6Me_6)Ru(\eta^5\text{-}Me_4T)^{2+}$ by Cp_2Co gives $(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}Me_4T)$, which is an analog of **10** [49], it too is not reported to isomerize to a ring-opened product similar to **11**.

The planar 6-membered ring in **11** has been described as an aromatic iridathiabenzene unit [55]. It forms η^6-complexes [57] and reacts with a variety of Lewis acids and bases [58]. With phosphines it forms adducts [eq. (14)] in which the iridium is coordinatively saturated and the 6-membered ring is no longer planar nor aromatic



(14)

[59]. Jones reported the formation of the Rh analog of **12** by the reaction shown in eq. (15) [60,61]. Detailed



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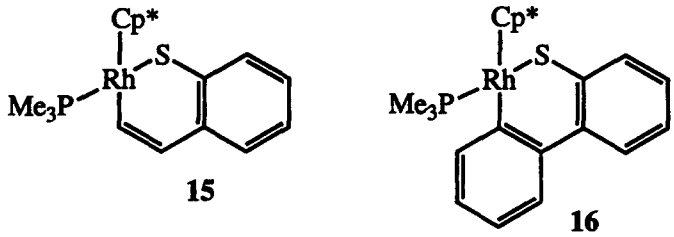
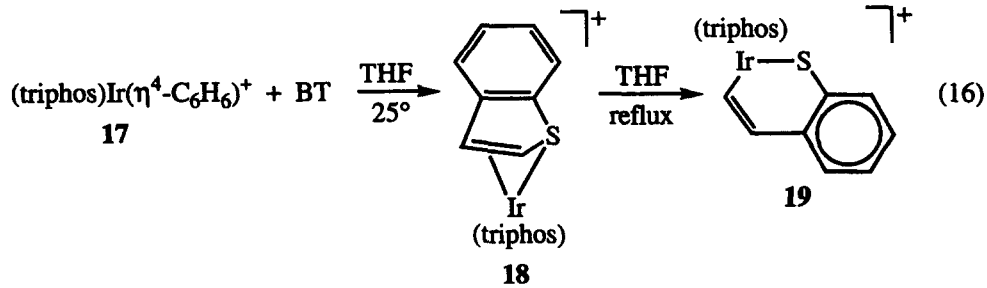


15 16

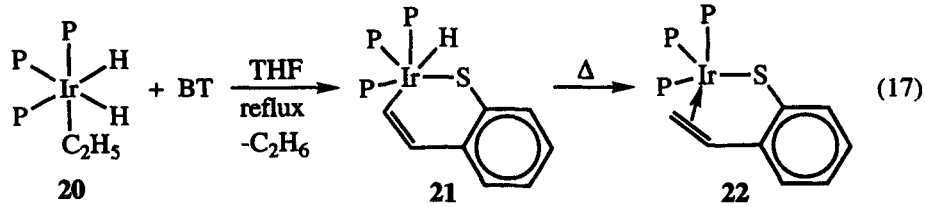
studies indicate that this reaction proceeds by reductive-elimination of benzene to give a 16-electron fragment $Cp^*Rh(PMe_3)$ that reacts with thiophene by C—H or C—S oxidative-addition to give either $Cp^*Rh(PMe_3)(H)$(thienyl) or **14** [eq. (15)]; complex **14** is the more stable isomer. Benzo[b]thiophene and DBT also react to form C—S inserted products, **15** and **16** [60,61]. A variety of methyl-substituted dibenzothiophenes undergo this reaction [62], but it is interesting that the sterically hindered 4,6-dimethyldibenzothiophene forms only an η^1(S) complex but not a C—S inserted product. The hydrotris(3,5-dimethyl-1-pyrazolyl)borate complex $Tp^*Rh(C_2H_4)(PMe_3)$ reacts either thermally or under UV-photolysis [63] like **13** in eq. (15) to give a mixture of C—H and C—S oxidative-addition products, $Tp^*Rh(PMe_3)(H)$(2-thienyl) and $Tp^*Rh(CHCHCHCHS)(PMe_3)$; however, in these complexes, the C—H oxidative-addition isomer is the more stable one.

Bianchini and Sánchez-Delgado describe ring-opening reactions of thiophene (T) [64] and benzo[b]thiophene (BT) [65] with the 14-electron fragment $(triphos)Ir^+$ that is generated by dissociation of benzene from $(triphos)Ir(\eta^4\text{-}C_6H_6)^+$; triphos is $MeC(CH_2PPh_2)_3$. In the reaction with BT, intermediate **18** was isolated and



(16)

assigned an η^3-BT structure based on spectroscopic studies. As in **11**, the Ir in **19** is part of a delocalized iridathiabenzene 6-membered ring. Reaction of **19** with H_2(5 atm) yields a sulfur-coordinated complex of 2-ethylbenzene thiolate resulting from hydrogenation of the C=C bond and cleavage of the Ir—C bond in **19** [65]. When the 16-electron fragment (triphos)Ir(H) is reacted with BT, the ring-opened product **21** is generated initially [eq. (17)] but is converted to the 2-vinylbenzenethiolate complex **22** on heating. Thiophene reacts with

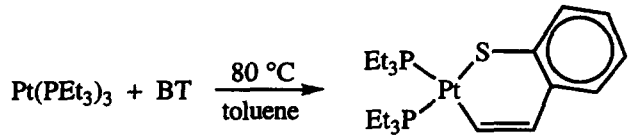


(17)

20 in the same manner to give the butadiene thiolate analog of **22** [64]. The 16-electron rhodium fragment (triphos)Rh(H), generated thermally from $(triphos)RhH_3$, undergoes many of the same reactions as (tri-

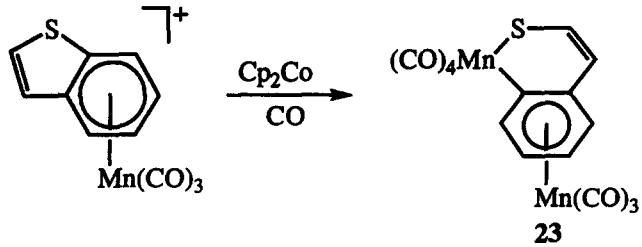
phos)Ir(H) with T [66,67] and BT [68]. In addition, the Rh analog of **22** *catalyzes* the conversion of BT to 2-ethylbenzenethiol [68]. This is the first example of a homogeneously catalyzed reaction of BT that results in cleavage of a C—S bond. Bianchini and Sánchez-Delgado [69] have also shown that DBT undergoes homogeneous HDS to give biphenyl and H_2S in the presence of catalytic amounts of (triphos)(H)Ir(η^2-C,S-$C_{12}H_8S$), a complex whose structure is analogous to that of **21** but contains the ligand resulting from C—S oxidative-addition of DBT to the (triphos)Ir(H) fragment. These catalyzed reactions are especially interesting because many of the mechanistic details of the reactions are understood. Homogeneous catalytic reactions of T, BT and DBT with H_2 have been recently summarized by Bianchini and Meli [70].

In another example of C—S oxidative-addition at an electron-rich iridium, T and BT were observed [71] to react with [Ir(1,5-COD)$(PMe_3)_3$]Cl to give ring-opened complexes $(Me_3P)_3$(Cl)Ir(SCHCHCHCH) and the chloro analog of **21**. Besides Ir and Rh, platinum in the electron-rich $Pt(PEt_3)_3$ reacts with T, BT and DBT to give C—S oxidative-addition products as illustrated for BT in eq. (18) [72]. In reactions that appear to be



(18)

quite different than those of the electron-rich Ir, Rh, and Pt complexes, $(CO)_3Mn(\eta^6\text{-BT})^+$ and $(CO)_3Mn(\eta^5\text{-T})^+$ are reduced by Cp_2Co in the presence of CO to give products [eqs (19) and (20)] in which Mn inserts into



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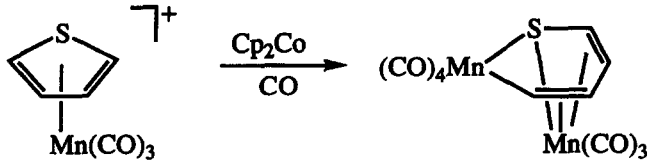
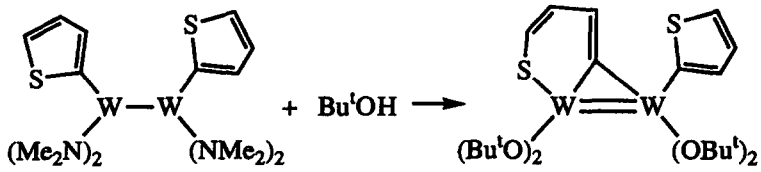


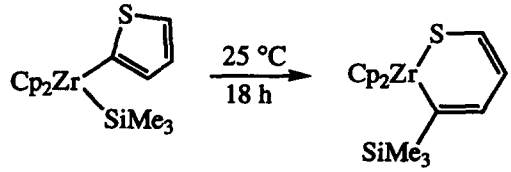
(20)

a C—S bond of the thiophene [73]; in product **23,** the metal has inserted into the S-aryl bond rather than the S-vinyl bond, which was observed for the Ir and Pt complexes [eqs (16)–(18)]. Another unexpected route [74] [eq. (21)] to a metal-inserted product involves C—S cleavage of a thienyl ligand to give a product in which a



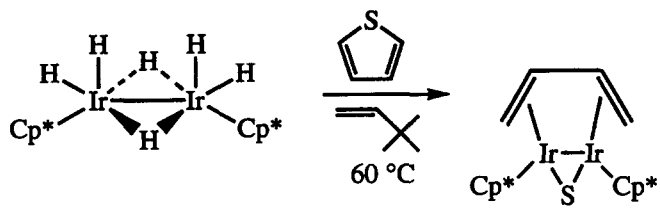
(21)

vinylidene of the cleaved thienyl ligand bridges two metals. Another interesting thienyl C—S cleavage reaction is that of the zirconium complex in eq. (22) [75].



(22)

In a remarkable reaction [eq. (23)] with thiophene, $[Cp^*IrH_3]_2$ not only cleaves both C—S bonds but also



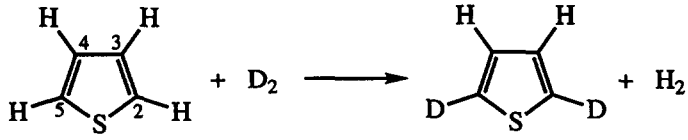
(23)

delivers two hydrogen atoms to form butadiene, which is stabilized by bonding to the iridium atoms [76]. The *t*-butylethylene presumably dehydrogenates the reacting $[Cp^*IrH_3]_2$ which provides an initial coordination site for the thiophene. Jones and Chin have also suggested a mechanism for the overall process [76].

The above reactions illustrate the many different ways that thiophene C—S bond cleavage occurs in transition metal complexes. Some of these reactions are better understood than others. Besides the reactions cited here, there are numerous others in which both C—S bonds in thiophenes are cleaved by mononuclear and polynuclear complexes; some of these have recently been summarized [70].

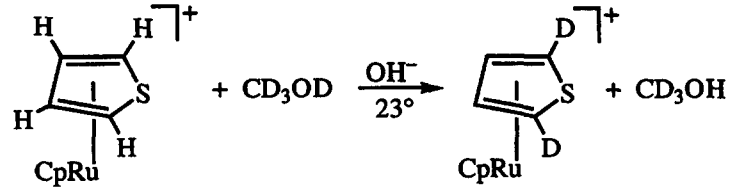
A few of the above reactions that result in C—S cleavage have been incorporated into mechanisms for HDS. While there is not space to describe them here, full discussions may be found in the following sources. Bianchini and Meli review mechanisms for catalytic hydrogenation and HDS of BT and DBT in the solution phase [70]. My group has proposed two mechanisms based on organometallic model studies. One [21, 22, 77] involves partial hydrogenation of thiophene to dihydrothiophene in the initial steps. The other [77, 78] begins with cleavage of both C—S bonds before any hydrogenation of the C_4H_4 portion of thiophene occurs. In order to test the viability of these and other mechanisms, we conducted [79] a series of thiophene HDS reactions using D_2 instead of H_2 over a $PbMo_6S_8$ catalyst and determined the number and location of deuterium atoms in the 1,3-butadiene product. It was concluded that both of the above hydrogenation and C—S cleavage mechanisms were consistent with the results. Of the mechanisms proposed in the literature that were not based on organometallic models, some were consistent with the findings; others were not [79]. A quite different approach to developing mechanisms of heterogeneous thiophene HDS was taken by Startsev [80,81]; his proposals are based on catalytic reactor and surface characterization studies.

Although the major focus of model studies has been on possible mechanisms for thiophene HDS, some attention has been devoted to understanding how the protons in thiophene and benzo[b]thiophene undergo exchange with D_2 in a process [eq. (24)] that is often much faster than desulfurization. This exchange has been



(24)

observed on $CoMo/\gamma\text{-}Al_2O_3$ [82] and $PbMo_6S_8$ [79]; exchange is much faster for protons in the 2 and 5 positions than in the 3 and 4 positions. This exchange could be explained by the model reaction in eq. (25) which

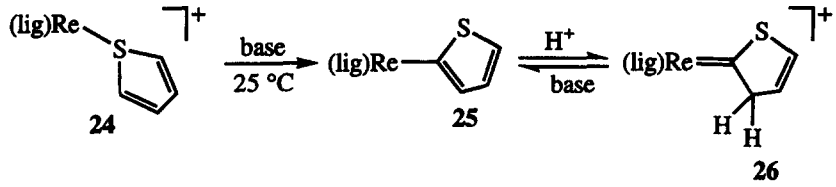


(25)

describes a base-catalyzed exchange of the 2,5-protons of an η^5-thiophene ligand with deuterium in deuteromethanol [83]. The reaction is first order in both the complex and OH^- concentrations; and it is much faster for protons at the 2 and 5 positions. On a $CoMo/\gamma\text{-}Al_2O_3$ catalyst, the oxide ions in Al_2O_3 may act as the base toward a thiophene that is η^5-coordinated to a Mo or Co. In fact, when $CpRu(\eta^5\text{-T})^+$ is adsorbed on an Al_2O_3 whose surface —OH groups have been exchanged with deuterium (—OD), the deuterium is incorporated into the 2 and 5 positions of the thiophene of the adsorbed $CpRu(\eta^5\text{-T})^+$ complex [83]. While η^5-coordination reasonably accounts for thiophene H–D exchange over HDS catalysts, η^6-coordination of BT does not [84]. On several HDS catalysts ($PbMo_6S_8$, $Co_{0.25}MoS$, and 5% $Re/\gamma\text{-}Al_2O_3$) exchange of BT protons with D_2 occurs

fastest at the 2 and 3 positions, but OH^--catalyzed exchange of the η^6-BT in $CpRu(\eta^6\text{-BT})^+$ occurs fastest in the 2 and 7 positions.

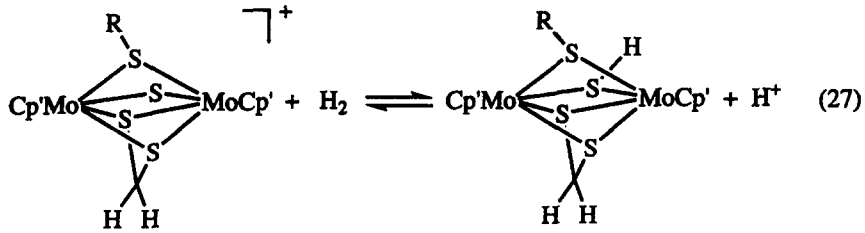
Another possible mechanism for H–D exchange could involve a thienyl intermediate. This proposal [85,86] is based on the reaction [eq. (26)] of $Cp(NO)(PPh_3)Re(\eta^1(S)\text{-T})^+$ (**24**) with bases that are at least as basic as



24 **25** **26** (26)

morpholine (pK_a = 8.3). Since free thiophene requires very strong bases for its deprotonation, the conversion of **24** to **25** is clearly promoted by the metal fragment; a possible mechanism for this reaction involves initial rearrangement of the η^1(S)-bonded thiophene to its 2,3-η^2(C,C) isomer, which is actually the species that undergoes deprotonation to give **25**. Reprotonation of **25** with acid (HBF_4 or TfOH) gives the carbene **26** which in some cases (e.g., 2-methylthiophene) rearranges rapidly to the more stable isomer **24**. The benzo[b]thiophene complex $Cp(NO)(PPh_3)Re(\eta^1(S)\text{-BT})^+$ undergoes [85,86] the analogous deprotonation and re-protonation reactions as in eq. (26) to give the benzothienylcarbene product. Unlike the Re system, the benzothienyl ligand in $Cp(PMe_3)_2Ru(\eta^1(C)$-benzothienyl) reacts [87] with CF_3SO_3H to give only the η^1(S)-benzothiophene complex $Cp(PMe_3)_2Ru(\eta^1(S)\text{-BT})^+$. Overall, the process involving deprotonation of thiophene and BT in their η^1(S) complexes to give η^1(C)-thienyl complexes [eq. (26)] followed by re-protonation back to the η^1(S)-thiophene complex, represents a possible mechanism for proton exchange with deuterium on an HDS catalyst.

In a mechanism proposed by Rakowski DuBois, the metal complex plays a quite different role [88]. It was observed that $[(\eta^5\text{-}C_5H_4Me)Mo]_2(S_2CH_2)(\mu\text{-S})(\mu\text{-SH})^+$ catalyzes the exchange [eq. (24)] of thiophene(T) and benzo[b]thiophene(BT) protons with D_2; moreover, preferential deuterium substitution occurs at the 2,5 positions in T and the 2,3 positions in BT. The authors provide convincing evidence that the catalyst serves simply to generate acid (H^+) in solution by a reaction similar to that in eq. (27) [89]. This heterolytic cleavage



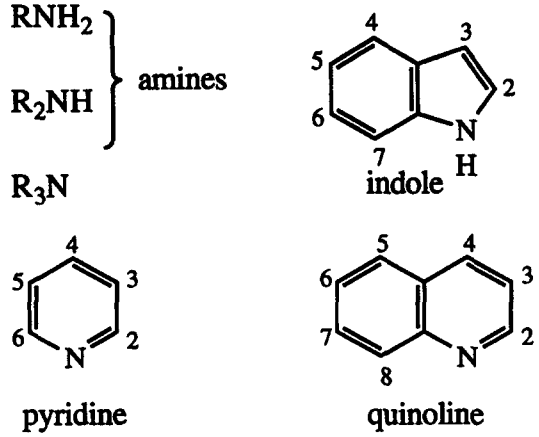
$R = CH_3, (CH_3)_2CH$ (27)

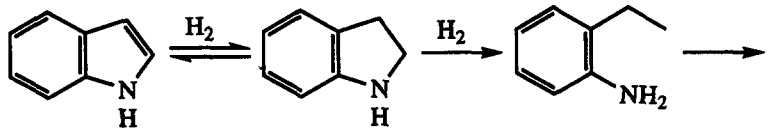
of H_2 is somewhat unusual because a H^- ion formally adds to a bridging sulfide to give a bridging SH group in the product. It is the D^+ product of this reaction, when using D_2, that is proposed to catalyze electrophilic substitution of hydrogens in the 2,5 sites on thiophene and the 2,3 positions of BT. Indeed, other deutero-acids such as D_2SO_4 also catalyze the exchange of the 2,5-protons in thiophene [90]. On a $CoMo/\gamma\text{-}Al_2O_3$ catalyst, one might conceive of a similar mechanism in which D_2 is converted to acidic D^+, perhaps as a surface —SD group which promotes the exchange reaction. At this point, there is no experimental evidence to distinguish among these different possible mechanisms [eqs (25), (26), (27)] for H–D exchange [eq. (24)] on HDS catalysts.

HYDRODENITROGENATION (HDN)

Organonitrogen compounds (Table 2) in petroleum feedstocks undergo hydrodenitrogenation to form ammonia according to eq. (2) [1,3,91]. The alkyl amines, both cyclic and non-cyclic, undergo HDN under milder conditions than the unsaturated pyridines, quinolines, pyrroles and indoles. A variety of catalytic reactor studies [1,3,13] indicate that the N-containing ring of unsaturated heterocycles must be saturated before C—N bond cleavage occurs. An example of this HDN process is shown with indole in eq. (28). Since the

Table 2. Types of organonitrogen compounds in petroleum

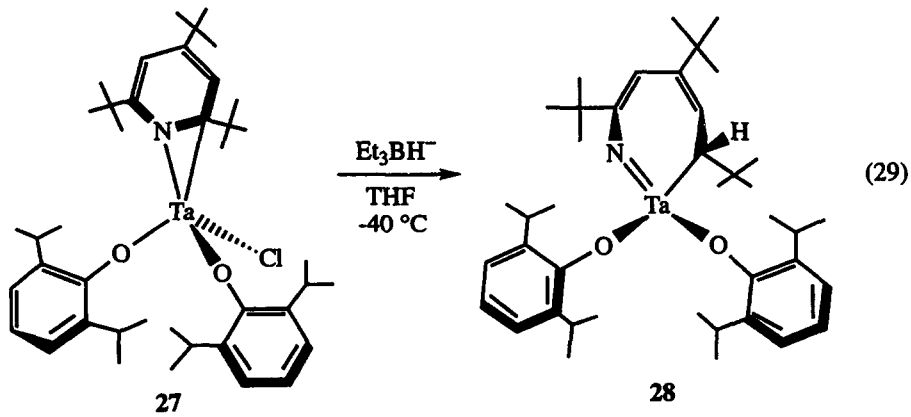




NH_3 + ethylbenzene + ethylcyclohexane

saturated amines undergo HDN rapidly, the overall HDN rates for the N-heteroaromatic compounds are determined by the rates of hydrogenation of the unsaturated N-containing rings. These rates decrease in the following order [1,92]: quinoline > pyridine > indole > pyrrole. Thus, as practiced, the HDN process consumes large quantities of relatively expensive H_2. One commercial goal for the HDN process is to find catalysts that will remove nitrogen as NH_3 without first hydrogenating the unsaturated N-containing rings. So, some of the organometallic modeling studies have been directed toward reactions that lead to C—N cleavage of unsaturated nitrogen heterocycles. Other studies have sought to understand HDN as now practiced, which means understanding mechanisms for the hydrogenation of unsaturated N-heterocycles and also mechanisms for C—N cleavage of the resulting saturated cyclic amines. Mechanisms for catalytic hydrogenation of the N-heteroaromatic compounds based on organometallic studies have been reviewed and discussed elsewhere [1,54,77,93]. Some of these hydrogenation studies were performed with single metal complexes [54], while others were done on metal cluster complexes especially those of Ru_3 and Os_3 [94–98]. Mechanisms for C—N cleavage in alkylamines, based primarily on reactions of secondary amines with Ru_3 and Os_3 carbonyl clusters, have been proposed [95]. Other approaches to HDN mechanisms are based on heterogeneous catalytic reactor studies [1,3,99–102].

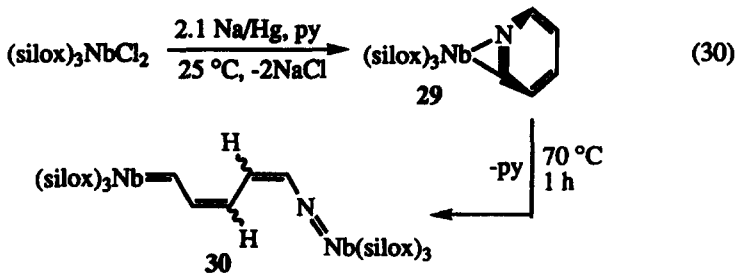
The goal of cleaving C—N bonds without prior hydrogenation of N-containing heteroarenes was recently achieved by Wigley and his group with a substituted pyridine [103], as shown in eq. (29). The η^2(N,C)-



27 28

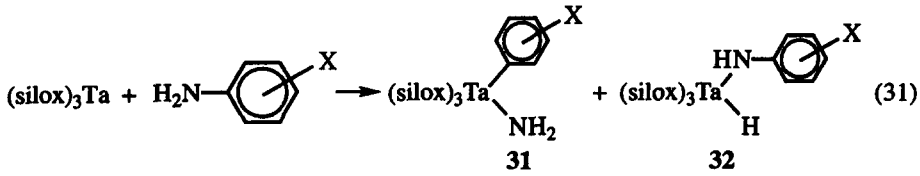
coordination of the tri(*t*-butyl)pyridine ligand in the starting complex **27** is important in promoting attack of H^- on the coordinated carbon. Although there were no identifiable intermediates in this reaction, the analogous reactions of **27** with carbon nucleophiles, RLi or RMgX, first give products resulting from the displacement of Cl^- by the alkyl or aryl R group. Several of these complexes with Ta—R groups have been isolated and fully characterized [103(b), 104]. Upon heating, the R group migrates from the Ta to the carbon of the η^2-tri(*t*-butyl)pyridine with concomitant cleavage of the C—N bond to give a complex analogous to **28** in which an R group replaces the hydrogen on the carbon bonded to Ta. Rate studies [104] of complexes with *p*-substituted phenyl R groups suggest that the R group acts as a nucleophile as it migrates from Ta to the carbon. Although details of the hydride reaction [eq. (29)] are not known, it too presumably proceeds by initial formation of a Ta—H bond followed by migration of the hydrogen to the carbon to give **28**. It is the formation of a strong Ta=N multiple bond that presumably provides the driving force for the C—N bond cleavage.

An even more recent and remarkable pyridine C—N bond cleavage [eq. (30)] was reported by Wolczanski



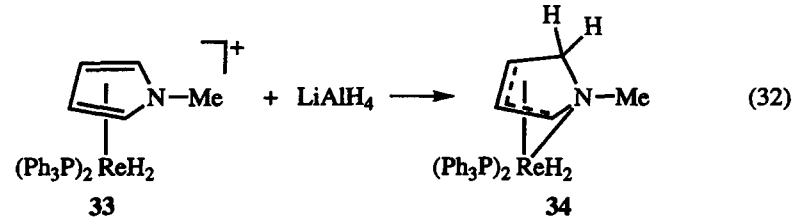
and co-workers [105]. In the first step, reduction of $(silox)_3NbCl_2$, where silox = Bu^t_3SiO, with Na/Hg in the presence of pyridine gives the η^2(N,C)-pyridine complex **29**. Thermolysis of this complex gives the ring-opened product **30** in which the cleaved C=N bond forms a Nb=C alkylidene complex with one Nb and a Nb=N imido complex with the other. Isomerization around the C=C double bonds gives 4 different isomers, one of which was characterized by an X-ray diffraction study. Although the mechanism is not known, this reaction suggests new ways to think about C=N cleavage without first hydrogenating the pyridine ring.

Reaction of $(silox)_3Ta$ with a series of substituted anilines is reported by Wolczanski to give products resulting from either C—N or N—H oxidative-addition [eq. (31)] [106]. The C—N oxidative-addition product



31 is favored by electron-withdrawing X groups, e.g., CF_3, whereas electron-donating X groups (Me or OMe) give exclusively the N—H oxidative-addition product **32**. This reaction is especially interesting because it demonstrates that it is possible to cleave C—N bonds even though the HDN of aniline requires hydrogenation of the arene ring before C—N cleavage occurs [1,107].

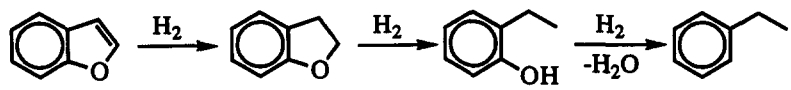
η^5-Coordinated N-methylpyrrole can be activated to attack by hydride in complex **33** to give **34**. Although this reaction does not lead to C—N bond cleavage, it resembles closely reactions [eqs. (9) and (11)] of η^5-



coordinated thiophene; one of these reactions [eq. (11)] leads to C—S bond cleavage. In the proper environment, it seems possible that an η^5-coordinated pyrrole could also undergo a similar ring-opening reaction. From the discussion above, it is evident that new organometallic models for C—N bond cleavage are beginning to emerge.

HYDRODEOXYGENATION (HDO)

Although oxygen content is usually low (<0.1%) in petroleum crudes, it is higher in shale oil, tar sand, and coal liquids [1]. The types of model organo-oxygen compounds that have been studied under catalytic conditions are primarily phenols and furans. As for HDS, pathways to HDO products [eq. (3)] can involve oxygen removal either before or after hydrogenation of the aromatic rings. An example of an HDO reaction that proceeds by initial hydrogenation is that of benzofuran [eq. (33)] [109]. The steps in this reaction are similar

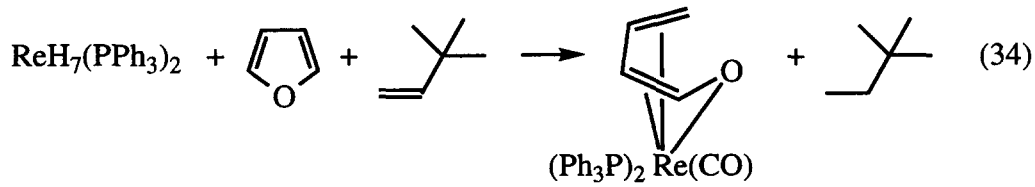


(33)

to those in the HDS of benzo[b]thiophene [37].

There are relatively few organometallic model studies that are directed toward understanding HDO. However, numerous C—O cleavage reactions of alkoxy or phenoxy ligands in transition metal complexes have been reported [110]; some of these might be considered as HDO models. The first step [eq. (33)] in the HDO of benzofuran (BF) has been modeled by its homogeneous hydrogenation to 2,3-dihydrobenzofuran using $(\eta^5\text{-}C_5Me_5)Rh(NCMe)_3^{2+}$ as the catalyst [54(a)]. As in the analogous hydrogenation of benzothiophene, this step presumably proceeds *via* 2,3-η^2 coordination of BF to a Rh—H intermediate followed by hydrogen transfer to give the 2,3-dihydrobenzofuran.

Furan itself appears to be a very weakly coordinating ligand [111]. To my knowledge, the only known η^5-furan complex is $(\eta^5\text{-}C_5Me_5)Ru(\eta^5\text{-}C_4H_4O)^+$, and it was reported to be insufficiently stable to be isolated [112]. An interesting reaction of furan that may be related to its HDO is that shown in eq. (34) [113]. This reaction,



(34)

35

which occurs in refluxing cyclohexane, gives complex **35** in 55% yield. The *t*-butylethylene presumably acts as a hydrogen acceptor to generate $ReH_3(PPh_3)_2$ which is the active intermediate that consumes two moles of furan, one to form the 1-oxapentadienyl ligand and the other to serve as the source of the CO ligand; propane and propene are also produced. While little is known about the details of this reaction, it is interesting that furan decomposes on Pd(111) [114] and on clean and sulfided molybdenum surfaces [115] to give CO as the major product. On Pd(111), the other products are H_2 and benzene, presumably derived from a C_3H_3 surface species. Under HDO conditions on a reduced and sulfided $CoMo/Al_2O_3$ catalyst at 400°C [108], furan gives the C_3 molecules propene and propane in addition to butenes and butane. The observation of C_3 products during the HDO of furan suggests that CO may also be a product, although not identified in the study [108]. The formation of CO and C_3 products in the organometallic [eq. (34)] and clean metal surface model studies may offer an opportunity to understand details of the mechanism of furan HDO.

CONCLUDING COMMENTS

In 1982 when we began our first experiments in organometallic modeling of thiophene HDS, the proposed mechanisms for this reaction were based on observed reaction products, assumed coordinating properties of thiophene (primarily through the sulfur), and a generous amount of imagination. Very little was known about modes of thiophene binding in metal complexes or reactions of coordinated thiophene that lead to cleavage of C—S bonds. Now, fourteen years later, the situation is quite different due to the efforts of several research groups. We know that thiophene is capable of binding to metals in several different ways, and there are many different reaction types that lead to cleavage of thiophene C—S bonds. As a result, it is possible to write several reasonable mechanisms for thiophene HDS. Of course, it is possible that none of these proposals represents the process as it occurs on an HDS catalyst. Thus, further model studies may open even newer ways of thinking about thiophene HDS. On the other hand, it is also important to try to link both organometallic and clean surface model studies to the reactions occurring in HDS reactors. Even simple questions about catalytic HDS have not been answered. Which, if any, of the known modes of thiophene binding in metal complexes occurs

on the catalyst surface? How are these binding modes influenced by the specific metal on the surface, the neighboring atoms around the metal and the oxidation state of the metal? Can we design metal sites on catalyst surfaces that favor binding modes which activate thiophene to undergo C—S cleavage? Clearly, we do not have useful answers to these questions. But we do have tentative answers, which should help us move in the direction of constructing more efficient HDS catalysts.

In addition to developing an understanding of current catalysts and preparing new heterogeneous catalysts, I think another goal, particularly for organometallic chemists, is the creation of homogeneous HDS catalysts. Successes in this direction have already been cited in this overview. These early results demonstrate that homogeneous HDS is possible; however, much more efficient and less expensive catalysts are required.

While HDS modeling studies have developed to the point where we can think about creating new catalysts, HDN modeling is at a much earlier stage. A broader understanding of organonitrogen ligand binding and C—N cleavage reactivity in organometallic complexes and on clean surfaces is still needed for the development of new catalytic HDN processes.

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