# Reactivity of the Bis(dihydrogen) Complex $[RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2]$ toward S-Heteroaromatic Compounds. Catalytic Hydrogenation of Thiophene

Andrzej F. Borowski,*,† Sylviane Sabo-Etienne,*,‡ Bruno Donnadieu,‡ and Bruno Chaudret‡

*Institute of Coal Chemistry, Polish Academy of Sciences, 5 Sowinskiego Street, 44-121 Gliwice, Poland, and Laboratoire de Chimie de Coordination du CNRS, 205 Route de Narbonne, 31 077 Toulouse Cedex 04, France*

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Room-temperature stoichiometric reaction of the bis(dihydrogen) complex $[RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2]$ (**1**) with thiophene leads to the formation of a new complex that has been isolated and characterized as an $\eta^4$-thioallyl complex $[RuH(\eta^4(S,C)\text{-}SC_4H_5)(PCy_3)_2]$ (**2**). This complex easily regenerates **1** upon treatment with dihydrogen and can be successfully used as a catalyst precursor in thiophene hydrogenation to 2,3,4,5-tetrahydrothiophene (THT). The reaction of **1** with 2-acetylthiophene leads to a regioselective 1,5-C−S bond splitting with formal hydrogenation of two double C═C bonds and coordination of a new 2-hexen-2-olato-3-thiolato ligand in an $\eta^2(O,S)$ mode to form $[RuH_2\{\eta^2(O,S)\text{-}C_6H_{10}OS\}(PCy_3)_2]$ (**3**). The new complex **3** has been characterized by $^1H$, $^{31}P$, and $^{13}C$ NMR studies including $^1H$ DPFGSE TOCSY, 2D-$^1H-^1H\{^{31}P\}$ COSY DQF, and the correlated $^{13}C-^1H$ HMQC LR spectra. The solid state molecular structure of **3** has been unequivocally determined by single-crystal X-ray structure analysis. The bis(dihydrogen) complex **1** is an effective catalyst precursor for the homogeneous hydrogenation of thiophene (T) to 2,3,4,5-tetrahydrothiophene (THT), 2-methylthiophene (2-MeT) to 2-methyltetrahydrothiophene (2-MeTHT), 2-acetylthiophene (2-AcT) to 1-(2-thienyl)ethanol (1-(2-Tyl)E), 2-thiophenecarboxaldehyde (2-TA) to 2-thiophenemethanol (2-TM), and benzo[*b*]thiophene (BT) to 2,3-dihydrobenzo[*b*]thiophene (DHBT) under mild conditions (80 °C, 3 bar $H_2$). Dibenzo[*b*,*d*]thiophene (DBT) is not reduced under these conditions due to the formation of the S-coordinated dihydrogen complex $[RuH_2(\eta^2\text{-}H_2)\{\eta^1(S)\text{-}C_{12}H_8S\}(PCy_3)_2]$ (**4**).



## Introduction

Catalytic hydrodesulfurization (HDS) of petroleum and other fossil fuel feedstock is an important industrial process employed to remove sulfur as $H_2S$ through reaction with dihydrogen. While most of the sulfur-containing molecules (especially saturated cyclic thioethers and thiols) are susceptible to HDS, molecules containing thiophene rings, especially those containing substituted benzothiophenes and dibenzothiophenes, are resistant to desulfurization. As a consequence, these species constitute the major pollutants in petroleum- and coal-derived fuels, contributing significantly to acid rain problems through formation of sulfur oxides ($SO_x$) upon combustion. HDS represents one of the largest volume industrial processes based on transition metal catalysis and is also aimed at preventing catalyst poisoning both in refinement processes and in automobiles.[1]

The complex chemical composition of crude oil and the difficulty in studying its HDS catalysis have led to the examination of model compounds structurally resembling sulfur contaminants in petroleum.[2] Soluble metal complexes serve as very good models for studying catalytic reactions occurring during the course of HDS processes, as mechanistic information can be readily achieved by the use of spectroscopic and other analytical methods. Many homogeneous systems based on transition metal complexes have been studied in hydrogenation reactions of sulfur-containing heteroaromatics.[3] There are numerous reports on the reactivity of sulfur-containing heteroaromatics with metal complexes that lead to the formation of products bearing coordinated heteroaromatic ligands.[2b,4] Reports on C−S bond scis-

* Corresponding author. E-mail: sabo@lcc-toulouse.fr.
† Institute of Coal Chemistry, Polish Academy of Sciences.
‡ Laboratoire de Chimie de Coodination du CNRS.

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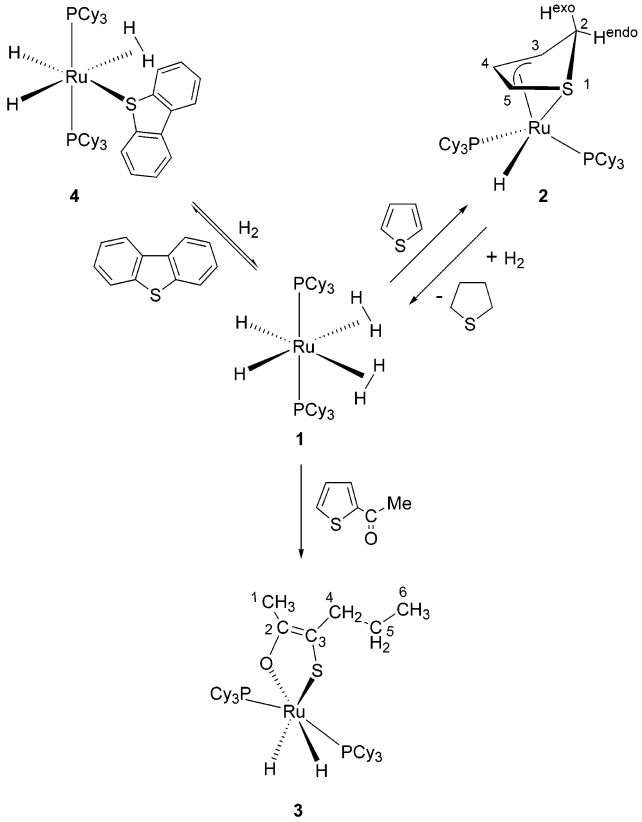
sion in heteroaromatic rings with formation of heterometallacycles are quite numerous.[5−11] Results of some successful hydrogenolyses of the C−S bond[7,8,12,13] and of genuine homogeneous HDS[13,14] and desulfurization reactions[9b,14,15] have been disclosed. In this context, ruthenium complexes play a significant role, but reports on their catalytic properties for hydrogenation of thiophenic substrates are scarce.[12b,16,17]

Our catalyst precursor $[RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2]$ (**1**) containing two labile dihydrogen ligands[18a,b] has been proven recently to be active and stable under mild hydrogenation conditions in arene hydrogenation reactions.[18c] Moreover, we have very recently reported the results of the reactivity of **1** with some selected nitrogen heteroaromatic compounds and its catalytic activity toward several N-heteroaromatics including hydrogenation of acridine.[18d] We now wish to present our results on the reactivity of **1** with some selected sulfur heteroaromatic compounds together with catalytic investigations on the hydrogenation of these S-aromatic compounds using **1** as a catalyst precursor.

**Scheme 1. Stoichiometric Reactions of 1 with Thiophene, 2-Acetylthiophene, and Dibenzo[*b*]thiophene**




## Results and Discussion

We will first describe the synthesis and characterization of three new complexes **2**−**4** resulting from the reactivity of the bis(dihydrogen) complex **1** with thiophene (T), 2-acetylthiophene (2-Act), and dibenzo[*b*,*d*]-thiophene (DBT), respectively. The reactions are depicted in Scheme 1. We will then report our results on the catalytic activity of **1** for hydrogenation of T, 2-AcT, and DBT, as well as 2-methylthiophene (2-MeT), 2-thiophenecarboxaldehyde (2-TA), and benzo[*b*]thiophene (BT). The role of **2**−**4** in the catalytic cycle will also be examined.

**Reaction of 1 with Thiophene (T). Preparation of $[RuH(\eta^4(S,C)\text{-}SC_4H_5)(PCy_3)_2]$ (2).** The reaction of **1** with 2 equiv of thiophene (T) in pentane leads to the formation of a beige solid analyzed as $[RuH(\eta^4(S,C)\text{-}SC_4H_5)(PCy_3)_2]$ (**2**). This complex is formulated as a neutral ruthenium(II) complex coordinating one hydride, two *cis* tricyclohexylphosphines, and a thioallyl ligand bound in an $\eta^4(S,C)$ fashion (see Scheme 1). The hydride is characterized in the $^1H$ NMR spectrum ($C_6D_6$, 293 K) by a doublet of doublets at $\delta$ −20.90 as a result of a coupling with two nonequivalent phosphorus nuclei ($J_{P-H}$ = 28 and 35 Hz). This signal is of equal intensity with five other signals at low field characterizing the thioallyl ligand. Three broad signals at $\delta$ 5.56, 5.31, and 2.71 are assigned to the allylic moiety, whereas a virtual triplet at $\delta$ 4.27 and a doublet at $\delta$ 3.73 are attributed to the methylene protons ($J_{H-H}$ = 9 Hz). The triplet at $\delta$ 4.27 is the only resonance showing an appreciable coupling to phosphorus ($J_{P-H}$ = 9 Hz). It is transformed into a doublet upon phosphorus decoupling. The $^{31}P$-



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{$^1$H} NMR spectrum (293 K) shows two broad signals at $\delta$ 61.7 and 53.0.

A few $\eta^4$-thioallyl complexes have been previously reported in the literature. In particular, the dihydride rhenium complex [$ReH_2(\eta^4$-$SC_4H_5)(PPh_3)_2$] was obtained by reaction of thiophene with the polyhydride [$ReH_7$-$(PPh_3)_2$] in the presence of 3,3-dimethyl-1-butene.[19] In our system, it is noteworthy that reaction was observed in the absence of any hydrogen acceptor. A mechanism involving initial coordination of T, as an $\eta^4$-diene, to an unsaturated metal center followed by an intramolecular hydrogenation to form the S-bound thioallyl complex has been postulated by Jones et al. for the rhenium complex.[19] A similar pathway was also invoked by Rauchfuss et al. for a ruthenium complex[20] and by Bianchini et al. for an iridium one.[4a] It seems thus reasonable to believe that formation of **2** in the reaction of thiophene with **1** may proceed through a similar mechanism.

Interestingly, bubbling dihydrogen through a $C_6D_6$ solution of **2** in an NMR tube restores **1**, characterized by $^1$H and $^{31}$P NMR data. Removal of the thioallyl ligand from the coordination sphere of the metal leads to free tetrahydrothiophene (THT) characterized by a broad triplet at $\delta$ 2.66 in the $^1$H NMR spectrum assigned to the four $H^{2,5}$ of THT, the second signal being hidden by the intense signals of $PCy_3$ protons resonating between $\delta$ 1 and 2.5.

**Reaction of 1 with 2-Acetylthiophene (2-AcT). Synthesis of [$RuH_2\{\eta^2(O,S)$-$C_6H_{10}OS\}(PCy_3)_2$] (3).** Our findings that T is readily reduced to THT in the process catalyzed by **1** (vide infra), along with the fact that electron-withdrawing substituents at the 2 or 3 position of thiophene are known to facilitate the C−S bond cleavage,[7c,9,10] led us to investigate the reaction of 2-acetylthiophene (2-AcT) with **1**, to achieve hydrogenolysis of the C−S bond. Reaction of **1** with 1 equiv of 2-AcT produces a red solid analyzed as [$RuH_2\{\eta^2$-$(O,S)$-$C_6H_{10}OS\}(PCy_3)_2$] (**3**) (see Scheme 1). The NMR spectra and a single-crystal X-ray analysis allow the formulation of the complex as a dihydride five-membered metallacycle with an O,S-bound ligand. The $^1$H NMR spectrum of **3** in $C_6D_6$ reveals a high-field resonance triplet at $\delta$ −10.37 ($J_{P-H}$ = 33 Hz). The $^{31}$P{$^1$H} NMR spectrum shows a singlet at $\delta$ 82.9 that transforms into a triplet ($J_{P-H}$ = 33 Hz) upon selective decoupling of the $PCy_3$ protons, in agreement with two hydrides coupled to two equivalent phosphorus atoms. Apart from the multiplets between $\delta$ 1.8 and 2.4, typical for $PCy_3$ protons, four other signals are present in the low-field region of the $^1$H NMR spectrum. The assignment was established by $^1$H−$^1$H{$^{31}$P} COSY (see Figure 1) and $^1$H TOCSY experiments. The $^1$H{$^{31}$P} NMR spectrum reveals the presence of two methyl groups at different chemical environment. A triplet at $\delta$ 1.16 belongs to a terminal methyl group of an aliphatic chain, while the singlet at $\delta$ 2.65 corresponds to a methyl group linked to a carbon bound to an oxygen and an alkene carbon atom. Two methylene ligands resonate as a triplet at $\delta$ 3.16 ($J_{H-H}$ = 7.1 Hz) and as a multiplet at $\delta$ 2.10 (partly obscured by the signals of $PCy_3$ protons). The $^{13}$C{$^1$H} NMR spectrum of **3** in $C_6D_6$ exhibits two

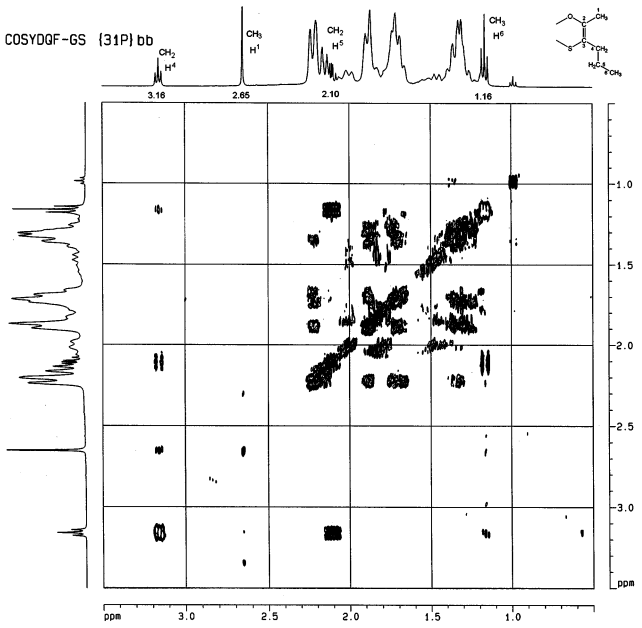


**Figure 1.** Selected region of the $^1$H−$^1$H{$^{31}$P} COSY spectrum of [$RuH_2\{\eta^2(O,S)$-$C_6H_{10}OS\}(PCy_3)_2$] (**3**) ($C_6D_6$, 293 K) showing $H^1$, $H^4$, $H^5$, and $H^6$ correlations.

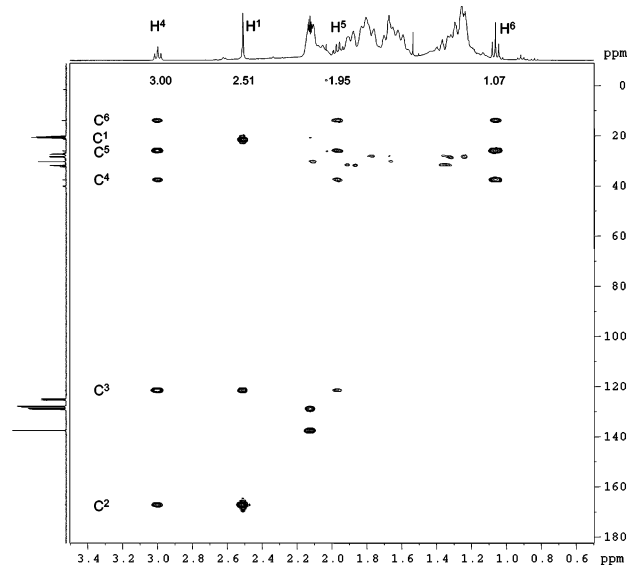


**Figure 2.** Selected region of the $^{13}$C−$^1$H HMQC LR spectrum of [$RuH_2\{\eta^2(O,S)$-$C_6H_{10}OS\}(PCy_3)_2$] (**3**) ($d_8$-toluene, 293 K) showing in particular long-range correlations of $C^2$ with $H^1$ and $H^4$ and of $C^3$ with $H^1$, $H^4$, and $H^5$.

signals in the region of methyl carbon resonances. The signal at $\delta$ 13.9 has been assigned to the terminal $C^6$ carbon of the aliphatic chain, while the lower field resonance signal ($\delta$ 21.7) belongs to the resonance of the methyl carbon ($C^1$) adjacent to the carbon atom bound to the oxygen. The two remaining aliphatic carbons resonate at $\delta$ 26.1 and 37.7, the latter being attributed to the signal of the methylene carbon ($C^4$) bound to the alkene carbon. The two alkene carbon atoms show resonance signals at $\delta$ 121.4 and 167.3, the former carbon atom ($C^3$) being bound to the sulfur atom. This assignment has been supported by a $^{13}$C−$^1$H HMQC LR experiment (see Figure 2).

Crystals of **3** suitable for an X-ray diffraction study (Table 1) were obtained from acetone solutions. The molecular structure is depicted in Figure 3. A few

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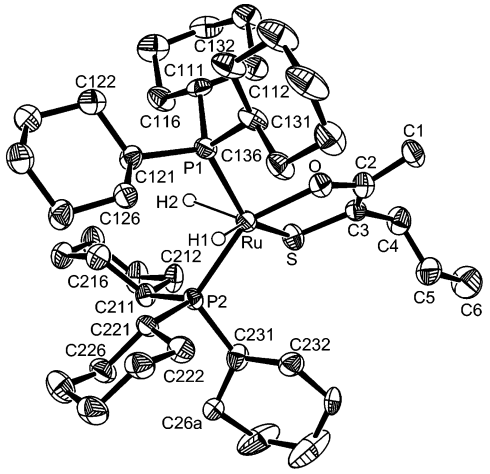


**Figure 3.** Molecular structure of $[RuH_2\{\eta^2(O,S)\text{-}C_6H_{10}OS\}(PCy_3)_2]$ (**3**). Selected bond lengths (Å) and angles (deg): Ru−O 2.033(5); Ru−S 2.281(2); Ru−P1 2.2930(18); Ru−P2 2.2976(18); Ru−H1 1.72(5); Ru−H2 1.73(5); S−C3 1.735(7); O−C2 1.363(8); C2−C3 1.336(10); C1−C2 1.483(11); C3−C4 1.509(9); C4−C5 1.490(11); C5−C6 1.515(10); O−Ru−S 81.44(14); P1−Ru−P2 116.53(7); H1−Ru−H2 103(3); P1−Ru−H1 63(2); P2−Ru−H2 74(2).

**Table 1. Crystal Data for $[RuH_2\{\eta^2(O,S)\text{-}C_6H_{10}OS\}(PCy_3)_2]$ (3)**

| | |
|---|---|
| formula | $C_{42}H_{78}OP_2SRu$ |
| fw | 794.11 |
| cryst syst | monoclinic |
| space group | $P2_1/c$ |
| Z, calcd density, $Mg/m^3$ | 4, 1.229 |
| abs coeff, $mm^{-1}$ | 0.518 |
| $F(000)$ | 1712 |
| $a$, Å | 9.9403(7) |
| $b$, Å | 43.1427(35) |
| $c$, Å | 10.0934(6) |
| $\beta$, deg | 97.576(8) |
| $V$, $Å^3$ | 4290.8(8) |
| temp, K | 180(2) |
| no. of data/restraints/params | 5763/13/451 |
| goodness of fit on $F^2$ | 0.904 |
| R1 [$I > 2\sigma(I)$] | 0.0504 |
| wR2 [$I > 2\sigma(I)$] | 0.0930 |
| R1 all data | 0.1173 |
| wR2 all data | 0.1142 |
| largest diff peak and hole, $e\cdot Å^{-3}$ | 0.594 and −0.494 |

complexes containing such a ligand coordinated in an $\eta^2$ mode by a sulfur and an oxygen bound to the same C=C function are known, and one crystal structure of a platinum complex was previously reported but with a selenium in place of sulfur.[21] The complex adopts a six-coordinate geometry in which the ligands lie in the vertexes of a slightly twisted trigonal prism, which is depicted in Figure 4. The central metal atom bound to a sulfur atom (Ru−S 2.281(2) Å) and to an oxygen atom (Ru−O 2.033 (5) Å) constitutes an element of a five-membered ring that includes as well the C(3)−S, C(2)−O, and C(2)−C(3) bonds. A *cis* arrangement has been found for the two $PCy_3$ ligands. This *cis* position is rare for such bulky phosphines but has been previously observed in a family of bis(silane)ruthenium complexes.[22] It should be noted that in that case the P−Ru−P angle was always close to 108°, whereas in **3**, a higher value is obtained (116.53(7)°). The C(3)−S and C(2)−O distances of 1.735(7) and 1.363(8) Å, respectively, are typical for interatomic distances between $sp^2$ carbons bound to sulfur and oxygen atoms.[23] The shortest carbon−carbon distance of 1.336(10) Å points toward a double C(2)=C(3) bond. These data indicate that the delocalization within the metallacycle is very limited, if it exists at all. Delocalization of RC(S)−C(S)R and −C(O)−C(O)− bonds and distortion from ideal trigonal prismatic and antiprismatic structures have been mentioned to occur in transition metal chelate complexes coordinating structurally analogous 1,2-dithiolene and tropolonate type ligands.[24] In such a case, C−O bond lengths are much shorter (1.308 Å in a cobalt complex coordinating 3-hydroxy-4-pyridinone), and delocalization is also evidenced by the elongation of the C−C bond (up to 1.412 Å, a value lying between a single C−C and a double C=C bond).[25] The Ru−O interatomic distance of 2.033(5) Å in our complex **3** is similar to that reported in a ruthenium phenoxide complex (Ru−O 1.982 Å)[26] and in another ruthenium complex coordinating a carboxylato fragment through only one C−O bond (Ru−O 2.012 Å).[27] The distances between the carbon atoms in the aliphatic chain of 1.505 Å (average) and the C−C−C bond angles of 114° are typical for that kind of bonding.[28] The shortest C−C single bond of 1.483(11) Å, localized between the methyl carbon C(1) and the alkene carbon C(2), is similar to that found in a ruthenium butadiene thiolate complex (1.46 Å).[29a]

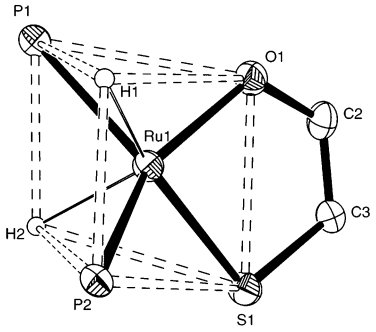


**Figure 4.** Partial molecular structure of **3** showing the trigonal prism.

In line with the above results, the reaction of 2-AcT with $[Ru(\eta^4\text{-COD})(\eta^6\text{-COT})]$ (the precursor used for the synthesis of **1** in the presence of depe (depe = 1,2-bis(diethylphosphino)ethane), studied by Komiya et al., leads also to a regioselective 1,5-insertion into the C−S bond.[10] However in that case, the formation of a thiaru-

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thenacycle [Ru{SC(COMe)=CHCH=CH}(depe)$_2$] is observed with a Ru−S bond of 2.427(2) Å, longer than in **3** (2.281(2) Å).

It should be noted that reaction of 2-AcT with **1** coordinating two dihydrogen molecules is a very clean reaction. The reaction is total, and **3** was isolated in very good yield (93%). Synthesis of this product requires the $C^5$−S bond cleavage in 2-AcT, formal hydrogenation of two C=C double bonds, and formation of a new C=C double bond. No other products are observed when the reaction is performed in an NMR tube and followed by $^1$H and $^{31}$P NMR spectroscopy.

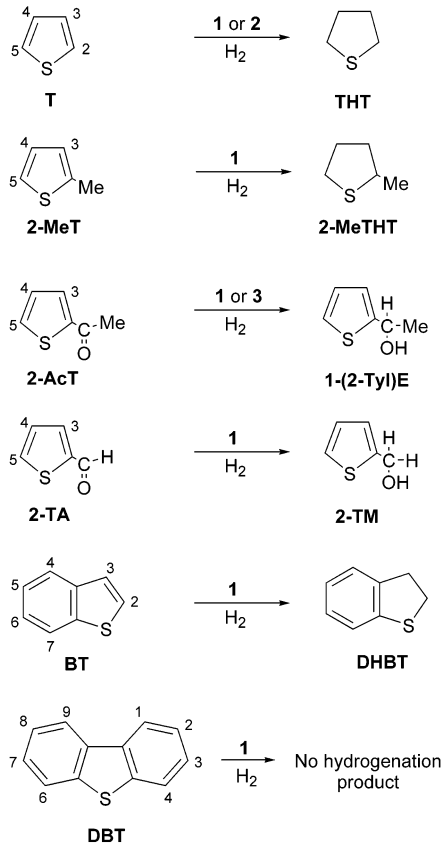
**Reaction of 1 with Dibenzo[*b,d*]thiophene (DBT). Characterization of [RuH$_2$($\eta^2$-H$_2$)($\eta^1$(*S*)-C$_{12}$H$_8$S)(PCy$_3$)$_2$] (4).** Reaction of **1** with dibenzo[*b,d*]thiophene (DBT) in pentane leads to the formation of a yellow-green solid. NMR studies indicate the formation of a new complex, **4**, contaminated with some unreacted **1** and free DBT. **4** was characterized as a dihydride(dihydrogen)(DBT) species, [RuH$_2$($\eta^2$-H$_2$)($\eta^1$(*S*)-C$_{12}$H$_8$S)(PCy$_3$)$_2$] (see Scheme 1). The $^1$H NMR spectrum shows a broad hydride resonance at $\delta$ −8.2 and four signals in the low-field region between $\delta$ 8.3 and 7.4. At 253 K the four signals of equal intensity are well-resolved. The multiplicities and chemical shifts (see Experimental Section) are very similar to those found for other complexes in which the DBT ligand is $\eta^1$(*S*)-bound to the metal.[4g,29b,c] Such a formulation is also consistent with the 2D-$^1$H−$^1$H{$^{31}$P} COSY spectrum of **4**. The ratio between the hydride and the DBT signals indicates the presence of four hydrogen atoms in the coordination sphere of the metal. $T_1$ measurements were performed using the inverse-recovery method. A $T_{1min}$ of 36 ms (400 MHz, $C_7D_8$) is observed at 253 K. No decoalescence was observed down to 193 K. These NMR data are in agreement with a dihydride(dihydrogen) formulation.[30]

Bubbling dihydrogen into a $C_7D_8$ solution of **4** for 10 min at room temperature resulted in total substitution of the bound DBT by $H_2$, leading thus to the recovery of the starting material **1**. The reaction was monitored by $^1$H and $^{31}$P NMR spectroscopies and showed no traces of any product resulting from DBT hydrogenation.

**Catalytic Studies.** The catalytic experiments were typically performed at 80 °C under 3 bar of $H_2$ in cyclohexane, using **1** as catalyst precursor with a catalyst/S-substrate ratio of 1:50. The mixture was maintained at 80 °C for 24 h. The composition of the resulting mixture was determined by GC−MS analysis and by NMR. The reactions are described in Scheme 2, and the results are summarized in Table 2.

Hydrogenation of T with **1** as catalyst precursor results in 85% conversion after 24 h and selective formation of tetrahydrothiophene (THT) (entry 1 of Table 2). Reduction of 2-methylthiophene (2-MeT) to 2-methyltetrahydrothiophene (2-MeTHT) proceeds at a much slower rate, as only 11% of 2-MeT is converted in the same conditions (entry 4). This might be attributed to the steric hindrance imposed by the methyl group at the $C^2$ carbon. A catalytic hydrogenation test of T was also performed in $d_{12}$-cyclohexane in the presence of **1** (see entry 2). Total conversion of T into THT was

**Scheme 2. Catalytic Activity of 1 toward S-Heteroaromatic Compounds**




observed (by GC and $^1$H NMR), and **1** was the only ruthenium species present in the reaction mixture, as detected by $^1$H and $^{31}$P NMR at the end of the experiment. It should be noted that, in this experiment, concentrations of **1** and T were 5 times larger as compared with those applied in the standard hydrogenation tests, thus allowing a total conversion of T into THT. We have shown above that reaction of **1** with a 2-fold excess of T leads to a formal elimination of two $H_2$ molecules and isolation of the new complex **2** incorporating a thioallyl ligand. We have also mentioned that **1** was regenerated by bubbling $H_2$ into a $C_6D_6$ solution of **2** with concomitant formation of THT. It was therefore straightforward to check the catalytic activity of **2**. Remarkably, when using **2** as catalyst precursor (entry 3) in the same conditions used with **1** (entry 1), a slightly higher conversion of T was obtained. This suggests the involvement of **2**, at least as a transient form, in a catalytic cycle for T hydrogenation. To the best of our knowledge, our findings represent the first example of a homogeneous hydrogenation of T to THT. The only previous report in connection to that work refers to an iridium system in which the S-bound thiophene complex [IrH($\eta^1$-SC$_4$H$_4$)$_2$(PPh$_3$)$_2$][PF$_6$] was hydrogenated to the corresponding THT complex [IrH($\eta^1$-SC$_4$H$_8$)$_2$(PPh$_3$)$_2$][PF$_6$].[4a] This reaction formally corresponds to two catalytic cycles. Another example of a stoichiometric hydrogenation of T to THT was also reported by thermolysis of the $\eta^4$-thioallyl complex [ReH$_2$($\eta^4$-SC$_4$H$_5$)(PPh$_3$)$_2$].[19] Also relevant to our work is the hydrogenolysis of T in drastic conditions (up to 60% conversion at 160 °C under 30 atm of $H_2$) catalyzed by the rhodium complex [(triphos)Rh($\eta^3$-SCH=CHCH=

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**Table 2. Hydrogenation of S-Aromatic Compounds[a]**

| entry | substrate | conversion (%) | products[b] | TON[c] |
|---|---|---|---|---|
| 1 | thiophene | 85 | THT | 42.5 |
| 2 | thiophene[d] | 100 | THT | 50 |
| 3 | thiophene[e] | 87 | THT | 43.5 |
| 4 | 2-methylthiophene | 11 | 2-MeTHT | 5.5 |
| 5 | 2-acetylthiophene | ca. 60 | 1-(2-Tyl)E | ca. 30 |
| 6 | 2-acetylthiophene[f] | 80 | 1-(2-Tyl)E | 40 |
| 7 | 2-acetylthiophene[g] | ca. 60 | 1-(2-Tyl)E | ca. 30 |
| 8 | 2-thiophene-carboxaldehyde | 90 | 2-TM | 45 |
| 9 | benzo[*b*]thiophene | 86 | DHBT | 43 |
| 10 | dibenzo[*b,d*]thiophene[h] | 0 | | 0 |

[a] Unless stated otherwise, **1** is the catalyst precursor. Conditions: 80 °C, 3 bar $H_2$, 24 h; solvent, cyclohexane (10 mL); [Ru] = $3 \times 10^{-3}$ M; [substrate] = 0.15 M, substrate/Ru = 50. The products were analyzed by GC/MS. [b] Products: THT = 2,3,4,5-tetrahydrothiophene; 2-MeTHT = 2-methyltetrahydrothiophene; 1-(2-Tyl)E = 1-(2-thienyl)ethanol; 2-TM = 2-thiophenemethanol; DHBT = 2,3-dihydrobenzothiophene. 100% selectivity for each product. [c] TON is defined as mole of product formed per mole of Ru. [d] Solvent: $d_{12}$-cyclohexane (2 mL), [Ru] = $15 \times 10^{-3}$ M, [substrate] = 0.75 M, thiophene/Ru = 50, reaction time 17 h. The products were analyzed by GC and $^1$H NMR. [e] [RuH($\eta^4$-$SC_4H_5$)($PCy_3$)$_2$] (**2**) was used as a catalyst precursor; concentrations and conditions as in footnote *a*. [f] Solvent: $d_{12}$-cyclohexane (2 mL), [Ru] = $15 \times 10^{-3}$ M, [substrate] = 0.75 M, 2-AcT/Ru = 50, reaction time 18 h. The products were analyzed by $^1$H NMR and GC/MS. [g] [$RuH_2$\{$\eta^2$(*O,S*)-$C_6H_{10}OS$\}($PCy_3$)$_2$] (**3**) was used as a catalyst precursor; concentrations and conditions as in footnote *a*. [h] Conditions as in footnote *a* but with a dihydrogen pressure of 20 bar.



$CH_2$)] in the presence of a strong base KO$^t$Bu. A mixture of 1-butanethiol, *n*-butane, and butenes was obtained.[7b] Interestingly, a complete desulfurization of T to *n*-butane was reported from the dimer [(Cp*IrHCl)$_2$] via a butanethiolate intermediate.[14c]

Hydrogenation of 2-AcT in the presence of **1** leads to the selective hydrogenation of the carbonyl group and formation of the secondary alcohol 1-(2-thienyl)ethanol (1-(2-Tyl)E), leaving the heteroaromatic ring intact as analyzed by GC/MS and $^1$H NMR. A 60% conversion of 2-AcT was obtained after 24 h of reaction at 80 °C under 3 bar of $H_2$ (entry 5). The formation of this alcohol was also confirmed by running an experiment in $d_{12}$-cyclohexane for in situ NMR measurements (entry 6 and see Experimental Section). As we have found in the previous case for catalytic thiophene hydrogenation by **1** or **2**, the isolated complex **3** resulting from the stoichiometric reaction of 2-AcT with **1** can also be used as catalyst precursor giving similar results (entry 7 versus 5). Similarly, reduction of the aldehyde group in 2-thiophenecarboxaldehyde (2-TA) leads to the formation of the corresponding primary alcohol 2-thiophenemethanol (2-TM) with 90% conversion as analyzed by GC/MS (entry 8).

As reported by other authors, drastic reaction conditions (170 °C, 110 bar $H_2$) are generally required to achieve hydrogenation of benzo[*b*]thiophene (BT) to 2,3-dihydrobenzo[*b*]thiophene (DHBT) with acceptable initial rates of ca. 6 TON/h.[3] When the reaction temperature is lowered to 85 °C and pressure reduced to 21 bar $H_2$, the initial hydrogenation rates are below 1 TON/h.[17b,31] In our system BT is selectively reduced to DHBT with an overal rate of 1.8 TON/h (86% conversion after 24 h) under our mild standard conditions (entry 9). Thus, BT hydrogenation into DHBT occurs at the same rate as T hydrogenation into THT. The isolated aromatic ring of DHBT is reluctant to undergo hydrogenation. We have observed similar results when testing tetralin or indoline hydrogenation in the presence of **1** under similar reaction conditions.[18c,d]

Although there are several examples of C−S bond scission with DBT followed by C−S insertion into the coordination sphere of the metal, and effective desulfurization of the activated DBT molecule under relatively mild conditions,[3,13−15] there are no examples of homogeneous hydrogenation of arene rings in DBT in the presence of soluble metal complexes. Likewise, our system does not show any activity in hydrogenation of DBT (at 80 °C, under 3 or 20 bar $H_2$), correspondingly to our previous findings for tetralin and 9,10-dihydroantracene.[18c] Nevertheless, we noted a color change from beige to yellow of the reaction mixture containing **1** and DBT under a dihydrogen atmosphere, thus suggesting the formation of a new product. Indeed, we have shown above that stoichiometric reaction of **1** and DBT affords the new dihydrogen yellow complex [$RuH_2$($\eta^2$-$H_2$)($\eta^1$(*S*)-$C_{12}H_8S$)($PCy_3$)$_2$] (**4**) in which the DBT ligand is coordinated to the metal via the sulfur atom. Such a coordination mode might be responsible for the fact that we could not observe any DBT hydrogenation.

## Summary

We have shown that the bis(dihydrogen) ruthenium complex **1** can activate several S-heteroaromatic compounds both stoichiometrically and catalytically. Activation is obviously dependent on the nature of the S-substrate, leading to new organometallic compounds presenting different coordination modes of the S-substrates. In the case of thiophene, we were able to isolate the product resulting from its coordination as a thioallyl-(hydride) complex **2** and to prove that both **1** and **2** serve as catalyst precursors for thiophene hydrogenation. The coordination of thiophene as a thioallyl ligand in **2** is probably responsible for the good performance of our catalysts. Indeed, this coordination mode lowers the aromatic resonance stabilization energy, allowing an easy thiophene hydrogenation into tetrahydrothiophene in mild conditions, whereas no hydrogenation of DBT was observed. It was known from the literature that the presence of thiophene substituents on the 2 or 3 positions favored the C−S bond cleavage. It was indeed what we observed by using 2-AcT, but in our case, the C−S bond cleavage resulted in the unexpected formation of **3**, a dihydride metallacycle with an O,S-bound ligand. When testing 2-AcT hydrogenation, we did not observe any hydrogenation of the aromatic ring, but

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reduction of the keto function into 1-(2-thienyl)ethanol was catalyzed by **1** and **3** under dihydrogen pressure. A similar reaction was observed for the reduction of 2-thiophenecarboxaldehyde into 2-thiophenemethanol.

## Experimental Section

**General Procedures.** All manipulations were carried out under argon using standard Schlenk-line techniques. All solvents were freshly distilled from standard drying agents and thoroughly degassed under argon prior to use. $RuCl_3 \cdot 3H_2O$ was purchased from Johnson Mattey Ltd., and all other reagents were purchased from Aldrich or Fluka and were used as obtained (except DBT, which was purified by sublimation) but degassed before use. Reaction products were analyzed by GC on a Hewlett-Packard 5890 apparatus fitted with a FID detector using a capillary column (30 mm × 0.32 mm) packed with cross-linked methyl silicone. GC/MS (EI, 70 eV) determinations were performed on an HP 5970 MSD apparatus fitted with the column of analogous characteristics. Homogeneity of the reaction mixtures has been confirmed by the test with liquid mercury, which is known to inhibit colloidal catalysis.[32] **1** was prepared by the published method,[33] and hydrogenations were performed as previously reported.[18c] Microanalysis were performed by the Laboratoire de Chimie de Coordination Microanalytical Service. Proton and phosphorus spectra were recorded on a Bruker AC 200 (at 200.132 and 81.015 MHz, respectively) and on an AMX 400 (at 400.130 and 161.985 MHz) apparatus. The $^{13}C$ NMR spectra were obtained by using a Bruker AMX 400 (100.624 MHz) spectrometer.

**[RuH($\eta^4$(*S*,*C*)-$SC_4H_5$)($PCy_3$)$_2$] (2).** After adding thiophene (0.024 mL, 0.3 mmol) to a suspension of **1** (0.100 g, 0.15 mmol) in pentane (2 mL), the color of the solution changed from beige to yellow-green. The suspension was stirred for 1 h, during which time a beige precipitate formed that was filtered off, washed with cold pentane (2 × 1 mL), and dried in vacuo. Yield: 0.096 g (77%). Anal. Calcd for $C_{40}H_{72}P_2SRu$: C, 64.26; H, 9.65. Found: C, 64.46; H, 9.52. $^1H$ NMR (200 MHz, $C_6D_6$, 293 K): $\delta$ 5.56 (brs, 1H, $H^5$), 5.31 (brs, 1H, $H^4$), 4.27 (pst, 1H, $H^{2(exo)}$, $J_{P-H}$ = 9.0 Hz), 3.73 (d, 1H, $H^{2(endo)}$, $J_H{}^{2(exo)}{}_{-H}{}^{2(endo)}$ = 9.0 Hz), 2.71 (brs, 1H, $H^3$), 2.5−1.1 (m, 66H, $PCy_3$), −20.90 (dd, 1H, $J_{P-H}$ = 28 and 35 Hz, Ru−H). $^{31}P\{^1H\}$ NMR (81 MHz): $\delta$ 61.7 (br) and $\delta$ 53.0 (br).

**[$RuH_2$\{$\eta^2$(*O*,*S*)-$C_6H_{10}OS$\}($PCy_3$)$_2$] (3).** An addition of 1 equiv of 2-acetylthiophene (0.164 mL, 0.15 mmol) to a suspension of **1** (0.100 g, 0.15 mmol) in pentane (14 mL) resulted in an immediate color change of the solution from the initial beige to violet and finally after ca. 5 min to deep red. This suspension was stirred overnight, and after filtration, the resulting red solution was evaporated to dryness, leading to the obtention of a dark red voluminous solid. Yield: ca. 0.11 g (93%). Anal. Calcd for $C_{42}H_{78}OP_2SRu$: C, 63.50; H, 9.90. Found: C, 63.35; H, 10.07. $^1H$ NMR (400 MHz, $C_6D_6$, 293 K): $\delta$ 3.16 (t, 2H, $J_{H-H}$ = 7.2 Hz, $^4CH_2$), 2.65 (s, 3H, $^1CH_3$), 2.10 (dt, 2H, $J_{H-H}$ = 7.2 Hz, $^5CH_2$), 1.16 (t, 3H, $J_{H-H}$ = 7.2 Hz, $^6CH_3$), 2.3−1.1 (m, 66H, $PCy_3$), −10.37 (t, 2H, $J_{P-H}$ = 33.3 Hz, Ru−$H_2$). $^{31}P\{^1H\}$ NMR (162 MHz): $\delta$ 82.9 (s). $^{13}C\{^1H\}$ NMR (100 MHz): $\delta$ 167.3 (s, $C^2O$), 121.4 (s, $C^3S$), 37.7 (s, $C^4H_2$), 26.1 (s, $C^5H_2$), 21.7 (s, $C^1H_3$), 13.9 (s, $C^6H_3$).

Crystals suitable for X-ray diffraction analysis were grown by dissolving the red solid in a small amount of acetone. The resulting solution was kept at room temperature for a few days.

**[$RuH_2$($\eta^2$-$H_2$)($\eta^1$(S)-$C_{12}H_8S$)($PCy_3$)$_2$] (4).** Complex **1** (0.100 g, 0.15 mmol) was stirred overnight with dibenzo[*b*,*d*]thiophene (0.042 g, 0.225 mmol) in pentane (4 mL) at room temperature. A yellow-green solid precipitated that was filtered off, washed with pentane (3 × 1.5 mL), and dried in vacuo. The solid was contaminated by some unreacted **1** and DBT. Any attempt to purify it by recrystallization failed, leading to decomposition. It was thus impossible to obtain any micronalytical data. $^1H$ NMR (400 MHz, $C_7D_8$, 253 K): $\delta$ 8.22 (d, 2H, $H^{1,9}$, $J_{H-H}$ = 8.0 Hz), 7.82 (d, 2H, $H^{4,6}$, $J_{H-H}$ = 7.9 Hz), 7.41 (vt, 2H, $H^{2,8}$, $J_{H-H}$ = 7.1 Hz), 7.25 (vt, 2H, $H^{3,7}$, $J_{H-H}$ = 7.5 Hz), 2.2−1.0 (m, 66H, $PCy_3$), −8.2 (br s, 4H, Ru−H). $^{31}P\{^1H\}$ NMR (162 MHz): $\delta$ 70.0 (s).

**1-(2-Thienyl)ethanol.** $^1H$ NMR (200 MHz, $d_{12}$-cyclohexane, 293 K): $\delta$ 7.31 (m, 1H, $H^5$), 7.08 (m, 2H, $H^{3,4}$), 5.20 (q, 1H, $J_{H-H}$ = 6,5 Hz, CH), 4.76 (br s, 1H, OH), 1.70 (d, 3H, $J_{H-H}$ = 6.5 Hz, $CH_3$). Comparisons can be made with data from ref 34.

**X-ray Data.** Data were collected at low-temperature ($T$ = 180 K) on a Stoe imaging plate diffraction system (IPDS) equipped with an Oxford Cryosystems cooler device. The crystal-to-detector distance was 70 mm, and 133 exposures were obtained with the crystal oscillating 1.5° in $\varphi$. The final unit cell parameters were obtained by least-squares refinement of 5000 reflections. No significant fluctuation of the intensity was observed. The structure was solved by direct methods using the program SIR92[35] and refined by least-squares procedures on $F^2$ using SHELXL-97.[36] All hydrogen atoms were located on a difference Fourier map, but they were introduced in calculations in idealized positions with an isotropic thermal parameter fixed at 20% higher than those of the carbon atoms to which they were connected. The hydrides were isotropically refined. All non hydrogen atoms were anisotropically refined. Least-squares refinements were carried out by minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $F_o$ and $F_c$ are the observed and calculated structure factors. A weighting scheme was used in the last refinement cycles, where weights are calculated from the following expression: $w$ = [weight] × [1 − ($\Delta(F)$/6$\sigma(F)$]$^2$. The model reached convergence with $R_w = [\sum w(||F_o| - ||F_c|)^2 / \sum(|F_o|)^2]^{1/2}$. The criteria for a satisfactory complete analysis were the ratios of rms shift to standard deviation being less than 0.1 and no significant features in final difference maps. All calculations were performed by using WinGX program version 1.64-04.[37] The molecules were drawn with the aid of ORTEP32,[38] and the atomic scattering factors were taken from *International Tables for X-Ray Crystallography*.[39]

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**Supporting Information Available:** X-ray structural data for **3** (CIF). NMR spectra of **4** before and after treatment with dihydrogen. This material is available free of charge via the Internet at http://pubs.acs.org.

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