

First example of opening and hydrogenation of 2,3-dihydrobenzo[*b*]thiophene to 2-ethylthiophenol assisted by a soluble metal complex

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Displacement of THF by dihydrobenzo[*b*]thiophene (DHBT) in [(triphos)Ir(H)₂(THF)]BPh₄ yields the η¹-S-DHBT adduct [(triphos)Ir(H)₂(η¹-DHBT)]BPh₄ which reacts in THF at room temperature with KOBu^t to give the neutral 2-vinylthiophenolate derivative (triphos)Ir(H)₂(η¹-*o*-S(C₆H₄)CH=CH₂) via C₂-S bond cleavage; the latter compound is hydrogenated under mild conditions (2 bar H₂, 80 °C) to the 2-ethylthiophenolate derivative (triphos)Ir(H)₂(*o*-S(C₆H₄)Et) and under harsh conditions (30 bar H₂, 160 °C) to free 2-ethylthiophenol and (triphos)IrH₃.

The hydrodesulfurization (HDS) of thiophenic molecules occurring in the course of the hydrotreating catalysis of petroleum feedstocks is a complex process whose mechanism is still quite speculative.¹ As is outlined in Scheme 1 for the model substrate benzo[*b*]thiophene (BT), the hydrogenation of thiophenes over heterogeneous catalysts may lead to the formation of hydrocarbons and H₂S via two principal mechanisms.

Kinetic studies at elevated H₂ pressures suggest that the reactions go through hydrogenated intermediates (Scheme 1, path a), especially with higher analogs of thiophene such as BT in which the electron density is less localized on the sulfur atom.² The prehydrogenation path has never been confirmed by the homogeneous modeling studies which are all consistent with the alternative hydrogenolysis route (Scheme 1, path b).³

The present paper constitutes a preliminary account of the first example of opening and hydrogenation of 2,3-dihydrobenzo[*b*]thiophene (DHBT) to 2-ethylthiophenol (ETP) assisted by a transition metal complex. C-S bond cleavage of tetrahydrothiophene (THT) has previously been found to occur on polymeric species.^{4,5} Notably, the C-S bond cleavage of THT in Cl₃W(μ-THT)WCl₃ was obtained by reaction with a nucleophile that remains attached to the C₂ carbon atom.⁴

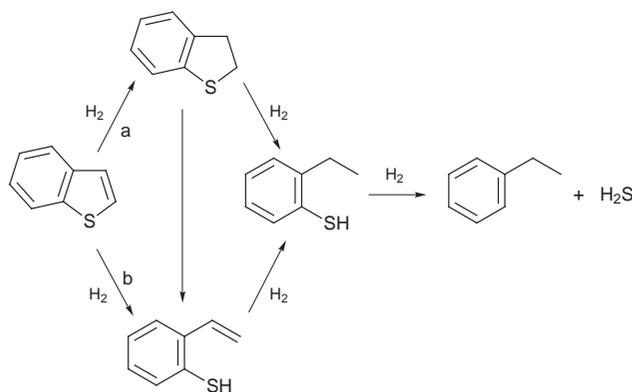
The iridium complex [(triphos)Ir(H)₂(η¹-DHBT)]BPh₄ **2** has been synthesized by adding a slight excess of DHBT to a tetrahydrofuran (THF) solution of [(triphos)Ir(H)₂(THF)]BPh₄ **1** [triphos = MeC(CH₂PPh₂)₃].[†] At room temperature, the reaction is quantitative even in THF as DHBT is a much better

ligand than THF. Very few η¹-DHBT complexes have been reported,⁷ but their existence has frequently been claimed in homogeneous and heterogeneous catalytic hydrogenation cycles of BT.^{1,2,3,7}

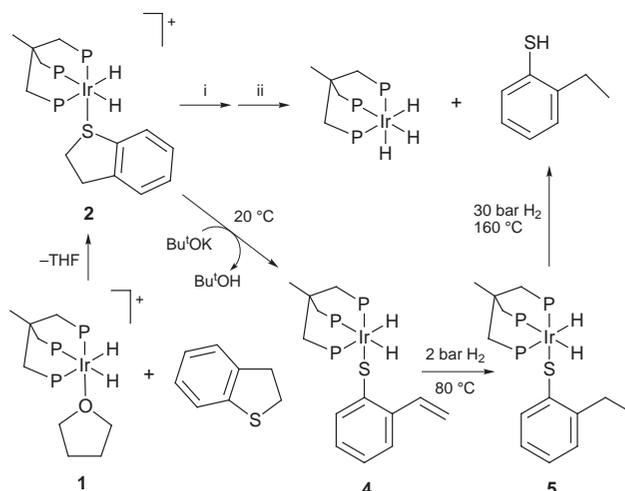
As shown in Scheme 2, the reaction of the η¹-S-DHBT adduct **2** in THF with an equivalent amount of KOBu^t at room temperature,⁸ followed by treatment with a high pressure of H₂ at 160 °C yields the hydrogenolysis product ETP and converts all the iridium precursor to the trihydride (triphos)IrH₃ **3**.⁹ The overall process was studied *in situ* by multinuclear NMR spectroscopy in THF-d₈ using a sapphire high-pressure NMR tube, initially under nitrogen and then under H₂.³ The strong base has been found to transform the DHBT ligand in **2** into a 2-vinylthiophenolate group yielding the neutral complex (triphos)Ir(H)₂(η¹-*o*-S(C₆H₄)CH=CH₂) **4**.[†] The tube was then pressurized with 2 bar of H₂. No reaction occurred at room temperature. Only at 80 °C, the ¹H NMR spectrum showed the signals of the vinyl hydrogens of **4** to decrease in intensity and the ³¹P NMR spectrum showed the appearance of a new AM₂ spin system. Within 15 h at 80 °C, all **4** converted to the known 2-ethylthiophenolate derivative (triphos)Ir(H)₂(*o*-S(C₆H₄)Et) **5**.¹⁰ Both **4** and **5** were isolated in the solid state by simply scaling up the NMR conditions. The hydrogen pressure in the tube was increased to 30 bar and the temperature was raised to 160 °C to observe a further chemical transformation: free 2-ethylthiophenol was formed quantitatively (¹H NMR, GCMS)^{3d} together with the known trihydride (triphos)IrH₃ **3**.⁹

The opening of the DHBT ligand by KOBu^t most likely occurs via an E₂ elimination as shown in Scheme 3(a).¹¹ Indeed, an E₂ elimination mechanism has been proposed to account for the hydrodesulfurization (HDS) of DHBT over the surface of real heterogeneous catalysts [Scheme 3(b)].¹²

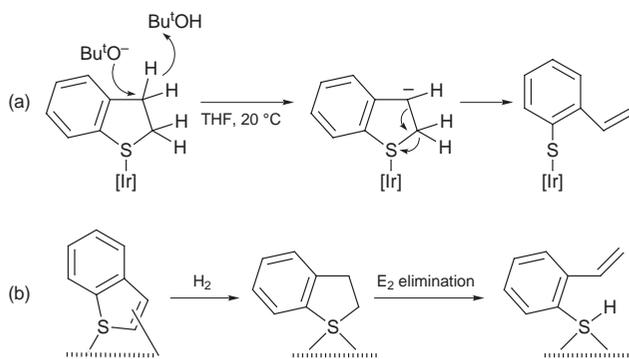
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Scheme 1 Principal mechanisms proposed for the HDS of benzo[*b*]thiophene over heterogeneous catalysts.



Scheme 2 Reagents and conditions: i, Bu^tOK, 20 °C; ii, 30 bar H₂, 160 °C.



Scheme 3 [Ir] = (triphos)Ir(H)₂.

Notes and references

† Satisfactory elemental analysis was obtained for all new compounds that were isolated as off-white microcrystals. *Selected spectroscopic data* for **2**: ³¹P{¹H} NMR (THF-d₈, 81.01 MHz) δ -2.4 (t, P_A), -15.8 (d, P_M), $J(\text{P}_A\text{P}_M)$ 17.8; ¹H NMR (THF-d₈, 200.13 MHz) δ 3.52 (m, DHBT), -9.35 (second-order dm, Ir-H); IR (Nujol mull) ν_{IrH} /cm⁻¹ 2074s.

For **4**: ³¹P{¹H} NMR (THF-d₈, 81.01 MHz) δ -0.5 (t, P_A), -25.4 (d, P_M), $J(\text{P}_A\text{P}_M)$ 13.6; ¹H NMR (THF-d₈, 200.13 MHz) δ 7.8 (masked, CH=CH_cH_i), 5.55 (dd, CH=CH_cH_i), 5.02 (dd, CH=CH_cH_i), -8.82 (second-order dm, Ir-H), $J(\text{HH}_c)$ 11.0, $J(\text{HH}_i)$ 17.6, $J(\text{H}_c\text{H}_i)$ 2.2; IR (Nujol mull) ν_{IrH} /cm⁻¹ 2055s.

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- In a blank experiment, a sample of DHBT in THF was treated with KOBu^t. The mixture was stirred for 6 h at room temperature but no reaction occurred.
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