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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)]BPh$_4$ yields the η^1-*S*-DHBT adduct [(triphos)Ir(H)$_2$(η^1-DHBT)]BPh$_4$ which reacts in THF at room temperature with KOBu^t to give the neutral 2-vinylthiophenolate derivative (triphos)Ir(H)$_2${η^1-*o*-S(C$_6$H$_4$)CH=CH$_2$} *via* C$_2$–S bond cleavage; the latter compound is hydrogenated under mild conditions (2 bar H$_2$, 80 °C) to the 2-ethylthiophenolate derivative (triphos)Ir(H)$_2${*o*-S(C$_6$H$_4$)Et} and under harsh conditions (30 bar H$_2$, 160 °C) to free 2-ethylthiophenol and (triphos)IrH$_3$.

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 H_2S *via* two principal mechanisms.

Kinetic studies at elevated H_2 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 polymetallic species.[4,5] Notably, the C–S bond cleavage of THT in Cl$_3$W(μ-THT)WCl$_3$ was obtained by reaction with a nucleophile that remains attached to the C$_2$ carbon atom.[4]

The iridium complex [(triphos)Ir(H)$_2$(η^1-DHBT)]BPh$_4$ **2** has been synthesized by adding a slight excess of DHBT to a tetrahydrofuran (THF) solution of [(triphos)Ir(H)$_2$(THF)]BPh$_4$[6] **1** [triphos = MeC(CH$_2$PPh$_2$)$_3$].† At room temperature, the reaction is quantitative even in THF as DHBT is a much better ligand than THF. Very few η^1-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 η^1-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 H_2 at 160 °C yields the hydrogenolysis product ETP and converts all the iridium precursor to the trihydride (triphos)IrH$_3$ **3**.[9] The overall process was studied *in situ* by multinuclear NMR spectroscopy in THF-d$_8$ using a sapphire high-pressure NMR tube, initially under nitrogen and then under H_2.[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)$_2${η^1-*o*-S(C$_6$H$_4$)CH=CH$_2$} **4**.† The tube was then pressurized with 2 bar of H_2. No reaction occurred at room temperature. Only at 80 °C, the ^{1}H NMR spectrum showed the signals of the vinyl hydrogens of **4** to decrease in intensity and the ^{31}P NMR spectrum showed the appearance of a new AM$_2$ spin system. Within 15 h at 80 °C, all **4** converted to the known 2-ethylthiophenolate derivative (triphos)Ir(H)$_2${*o*-S(C$_6$H$_4$)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 (^{1}H NMR, GCMS)[3*d*] together with the known trihydride (triphos)IrH$_3$ **3**.[9]

The opening of the DHBT ligand by KOBu^t most likely occurs *via* an E$_2$ elimination as shown in Scheme 3(a).[11] Indeed, an E$_2$ 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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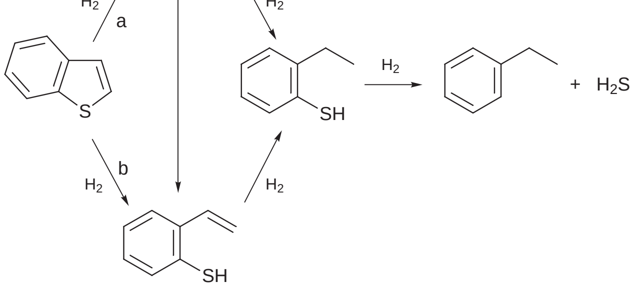
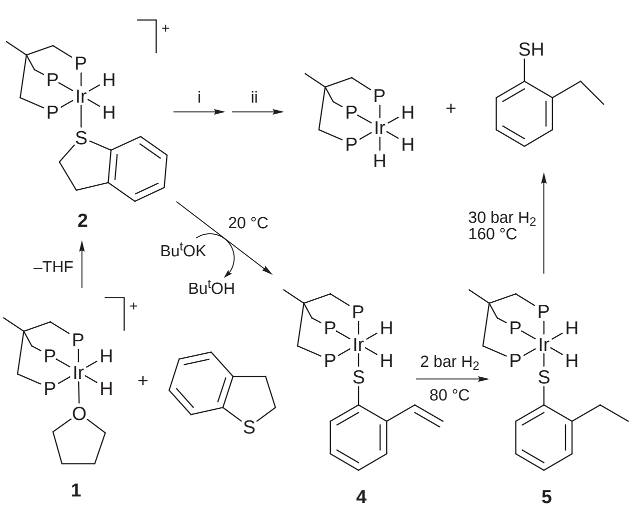
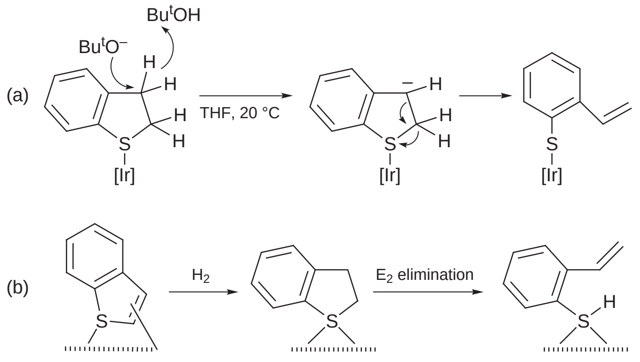


Scheme 1 Principal mechanisms proposed for the HDS of benzo[*b*]thiophene over heterogeneous catalysts.



Scheme 2 *Reagents and conditions*: i, Bu^{t}OK, 20 °C; ii, 30 bar H$_2$, 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**: ^{31}P{^{1}H} NMR (THF-d$_8$, 81.01 MHz) δ −2.4 (t, P$_A$), −15.8 (d, P$_M$), J(P$_A$P$_M$) 17.8; ^{1}H NMR (THF-d$_8$, 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**: ^{31}P{^{1}H} NMR (THF-d$_8$, 81.01 MHz) δ −0.5 (t, P$_A$), −25.4 (d, P$_M$), J(P$_A$P$_M$) 13.6; ^{1}H NMR (THF-d$_8$, 200.13 MHz) δ 7.8 (masked, C*H*=CH$_c$H$_t$), 5.55 (dd, CH=CH$_c$*H*$_t$), 5.02 (dd, CH=C*H*$_c$H$_t$), −8.82 (second-order dm, Ir–H), J(HH$_c$) 11.0, J(HH$_t$) 17.6, J(H$_c$H$_t$) 2.2; IR (Nujol mull) ν_{IrH}/cm^{-1} 2055s.

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