Hydrodesulfurization Model Systems. Homogeneous and Heterogeneous (Solid–Gas) Hydrogenation of Benzothiophene at Iridium

Claudio Bianchini,[*,†] Andrea Meli,[†] Maurizio Peruzzini,[†]
Francesco Vizza,[†] Piero Frediani,[‡] Verónica Herrera,[§] and
Roberto A. Sanchez-Delgado[*,§]

Istituto per lo Studio della Stereochimica ed
Energetica dei Composti di Coordinazione
CNR, 50132 Firenze, Italy
Dipartimento di Chimica Organica
Università di Firenze
50121 Firenze, Italy
Instituto Venezolano de Investigaciones Cientificas
IVIC, Caracas 1020 A, Venezuela

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Benzo[*b*]thiophene (BT) is a particularly interesting substrate since it represents one of the most abundant and refractory compounds in heavy oils. It is believed that hydrodesulfurization (HDS) of BT over solid catalysts involves the selective hydrogenation to 2,3-dihydrobenzo[*b*]thiophene (DHBT) prior to desulfurization to give ethylbenzene.[1] Indeed, some studies of homogeneous hydrogenation of BT to DHBT have recently been reported.[2] In contrast, only one example of metal-assisted opening and hydrogenation of BT has been described so far. Rauchfuss reacted BT with an iron cluster ($Fe_3(CO)_{12}$), obtaining the benzothiaferrole $Fe_2(C_8H_6S)(CO)_6$, which was subsequently hydrogenated to give primarily ethylbenzene together with some 2-ethylbenzenethiol, bis(2-ethylphenyl) sulfide, and bis(2-ethylphenyl) disulfide.[3]

In this paper we report the selective hydrogenation of complexed BT to 2-ethylbenzenethiolate ligand assisted by a mononuclear metal complex in either homogeneous or heterogeneous (solid–gas) fashion. Also, we describe the first X-ray structure of a mononuclear metallabenzothiabenzene complex.[4]

Stirring a tetrahydrofuran (THF) solution of the η^4-benzene complex [(triphos)Ir(C_6H_6)]BPh_4[5] (**1**) with a six-fold excess of BT at reflux temperature under nitrogen for 20 h produces an orange-red solution from which brick red crystals of [(triphos)Ir(η^2-*C,S*-C_8H_6S)]$BPh_4\cdot 1.5THF\cdot 0.5EtOH$ (**2**) are obtained in excellent yield (90%) by addition of ethanol (Scheme I) [triphos = $MeC(CH_2PPh_2)_3$].[6] The molecular structure of the complex cation in **2** is shown in Figure 1.[7] The coordination geometry around iridium may be described as either a distorted square-pyramid or a trigonal-bipyramid, the metal center being surrounded by three phosphorus atoms of triphos and by a carbon and a sulfur atom from a C–S-cleaved BT molecule. The bond distances between iridium and the atoms C_6 and S_1 [2.07(1) and 2.243(3) Å, respectively] match well those found by Angelici for the iridathiabenzene complex Cp*Ir(η^2-*C,S*-2,5-Me_2T).[8] The bond distances within the planar six-membered metallaring are suggestive of a delocalized π-bonding system, which is confirmed by the NMR data.[6,8]

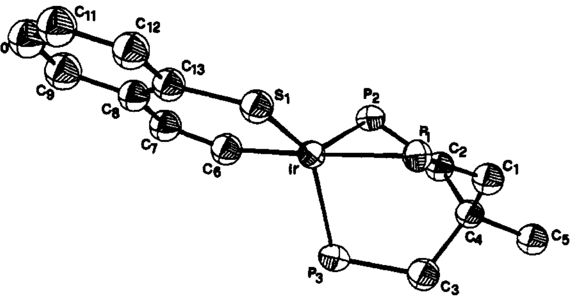
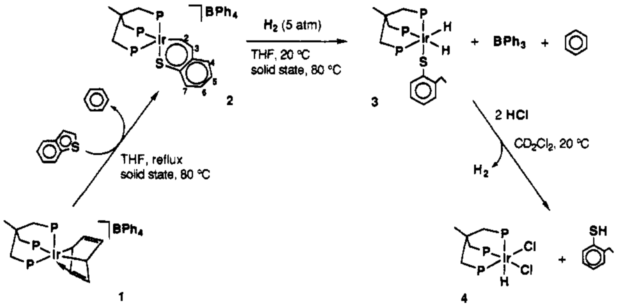


Figure 1. ORTEP drawing of the complex cation in **2**. All of the hydrogen atoms and phenyl rings of triphos are omitted for clarity. The relevant geometric features are as follows: IR–P_1 2.395(3), Ir-P_2 2.265(3), Ir–P_3 2.260(3), Ir–S_1 2.243(3), Ir–C_6 2.07(1), S_1–C_{13} 1.71(1), C_6–C_7 1.36(2), C_7-C_8 1.44(1), C_8–C_9 1.43(2), C_8-C_{13} 1.41(1), C_9–C_{10} 1.36(2), C_{10}-C_{11} 1.34(2), C_{11}-C_{12} 1.40(2), and C_{12}-C_{13} 1.40(2) Å; P_1-Ir-P_2 88.5(1), P_1-Ir-P_3 89.8(1), P_1-Ir-S_1 87.6(1), P_1-Ir-C_6 177.7(3), P_2-Ir-P_3 86.9(1), P_2-Ir-S_1 136.5(1), P_2-Ir-C_6 90.6(3), P_3-Ir-S_1 136.3(1), P_3-Ir-C_6 92.3(3), and S_1-Ir-C_6 91.6(3)°.

Scheme I



Interestingly, unsolvated **2** can simply be obtained by heating a solid–solid mixture of **1** and BT (1:10) at 80 °C for 3 h (yield 100%).[9]

Reaction of **2** with H_2 in either the solid state (5 atm H_2, 80 °C, 3 h) or THF solution (5 atm H_2, 20 °C, 3 h) results in the quantitative conversion to [(triphos)Ir(H)$_2${*o*-S(C_6H_4)C_2H_5}] (**3**), which is recovered as off-white microcrystals.[10] In the course of the reactions, the tetraphenylborate counteranion degrades to BPh_3 and benzene.[11] A related hydrogenation reaction of an iridathiabenzene complex, namely Cp*Ir(η^2-*C,S*-2,5-Me_2T), has

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[†] I.S.S.E.C.C., CNR, Firenze.

[‡] Dipartimento di Chimica Organica, Università di Firenze.

[§] IVIC, Caracas.

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(6) $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 81.01 MHz): 20 °C, A_3 spin system, δP –0.49 (br s); –70/–90 °C, AM_2 spin system, δP_A –11.23, δP_M 4.87, $J(P_AP_M)$ = 14.6 Hz. ^1H NMR (CD_2Cl_2, 20 °C, 600.14 MHz): δH_4 8.46 (br d, $J(H_4H_6)$ = 1.4 Hz, $J(H_4H_5)$ = 7.6 Hz), δH_2 8.33 (dq, $J(H_2H_3)$ = 11.2 Hz, $J(H_2P)$ = 7.0 Hz), δH_3 8.26 (m, $J(H_3P)$ = 5.8 Hz), δH_7 7.83 (dd, $J(H_7H_6)$ = 7.9, $J(H_7H_5)$ = 1.6 Hz), δH_6 7.74 (br t, $J(H_6H_5)$ = 7.3 Hz), δH_5 7.63 (td). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C, 50.32 MHz): δC_2 162.06 (q, $J(C_2P)$ = 21.1 Hz), δC_7 134.32 (s), δC_4 ca. 133 (masked by phenyl carbon resonances of either triphos or the BPh_4^- anion), δC_3 129.92 (s), δC_6 128.47 (s), δC_5 127.11 (s). Assignment of chemical shifts and coupling constants was done on the basis of $^1H\{^{13}P\}$, ^{13}C DEPT, $^1H,^1H$ 2D-COSY, and $^{13}C,^1H$ 2D-HETCOR NMR experiments.

(7) Crystal data: triclinic, space group *P*1, a = 17.391(3) Å, b = 16.957(4) Å, c = 12.795(3) Å, α = 77.51(2)°, β = 80.98(2)°, γ = 75.50(2)°, Z = 2, d_{calcd} = 1.31 g cm^{-3}, n_{obsd} = 7636, R = 0.072. THF and ethanol solvent molecules were located in the cell. Ethanol and one of the THF solvent molecules were assigned a population factor of 0.5.

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(9) At 80 °C, BT is a liquid whereas **1** is a solid. It is, however, difficult to state whether the reaction is truly heterogeneous or some **1** dissolves in the BT melt (homogeneous system).

(10) $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C, 81.01 MHz): AM_2 spin system, δP_A –2.31, δP_M –25.28, $J(P_AP_M)$ = 14.4 Hz. ^1H NMR (CD_2Cl_2, 20 °C, 200.13 MHz): δ –9.17 (second-order doublet of multiplets, AA′XX′Y spin system, $|J(AX) + J(AX')|$ = 132.6 Hz, $J(AY)$ = 12.1 Hz, Ir–*H*), δ 1.16 (t, $J(HH)$ = 7.5 Hz, CH_2CH_3), δ 2.84 (q, CH_2CH_3).

(11) Triphenylboron was extracted either by sublimation or with *n*-pentane and authenticated by ^1H NMR.

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recently been reported by Angelici.[12] In this case, however, the reaction at room temperature stops at the stage of oxidative addition of H_2, whereas in refluxing hexane, decomposition to uncharacterized products was observed.

Protonolysis of **3** in CD_2Cl_2 at room temperature with a 2-fold excess of gaseous HCl quantitatively affords [(triphos)IrH(Cl)$_2$][13] (**4**) and 2-ethylbenzenethiol (^{1}H NMR, GC/MS).

Certain of these results deserve further comment: (i) The hydrogenation of **2** to **3** formally requires five H atoms. Since we use a source of pairs of hydrogen atoms, it is reasonable to think of a heterolytic splitting of H_2 occurring at some stage of the reaction. Indeed, the production of H^+ well accounts for the conversion of BPh_4^- to BPh_3 and benzene.[14] Although detailed studies appear definitely necessary to establish at which stage the heterolytic splitting would occur, it is very much likely that this reaction takes place just in the initial interaction of **2** with H_2. In this respect, it may be useful to recall that heterolytic splitting of H_2 is easily promoted by a family of 1,1-dithio complexes of the formula [(triphos)Rh(S_2CX)]BPh_4 (X = O, S, NPh), which, like **2**, are characterized by π-delocalization over the metallacycle.[15] (ii) The *solid–gas* hydrogenation of BT confirms of the ability of organometallic fragments,[16] and in particular of [(triphos)Ir],[16a] to assist heterogeneous hydrogenation of unsaturated ligands or substrates. (iii) Even though no desulfurization of BT occurs in the experimental conditions of this work, unambiguous evidence has been provided for both homogeneous and heterogeneous hydrogenation of the thiophenic molecule after and not prior to its opening.

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Supplementary Material Available: Experimental details of the synthesis and characterization of the new complexes described in this paper; X-ray crystallographic data for **2** including experimental details, tables of selected distances and angles, atomic coordinates, and thermal parameters, and an ORTEP drawing with the phenyl substituents (13 pages); listing of observed and calculated structure factors (43 pages). Ordering information is given on any current masthead page.

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