Hydrodesulfurization (HDS) Model Systems. Opening, Hydrogenation, and Hydrodesulfurization of Dibenzothiophene (DBT) at Iridium. First Case of Catalytic HDS of DBT in Homogeneous Phase

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The kinetic selectivity for C–H vs C–S activation of dibenzothiophene (DBT) by the [(triphos)IrH] fragment has been observed upon either thermolysis of (triphos)Ir(H)$_2$(C$_2$H$_5$) in THF in the temperature range from 70 to 160 °C or dehydrohalogenation of (triphos)Ir(H)$_2$Cl with *t*-BuLi at room temperature [triphos = MeC(CH$_2$PPh$_2$)$_3$]. C–H bond cleavage already occurs at 20 °C to give as many as three isomeric DBTyl complexes of the formula (triphos)Ir(H)$_2$(DBTyl). The kinetic preference follows the order 3-DBTyl > 4-DBTyl ≥ 2-DBTyl, while the thermodynamic stability is in the order 4-DBTyl > 3-DBTyl > 2-DBTyl. Both C–H insertion and C–S insertion occur in the temperature range from 120 to 160 °C. Above the latter temperature, C–S insertion prevails over C–H insertion, and the complex (triphos)IrH(η^2-*C,S*-DBT) (**5**) is generated quantitatively. By reaction with H$_2$ (THF, 170 °C, 30 atm of H$_2$, 4 h), **5** is converted to a 31:69 mixture of the 2-phenylthiophenolate dihydride (triphos)Ir(H)$_2$(SC$_{12}$H$_9$) (**7**) and the trihydride (triphos)Ir(H)$_3$ (**8**) while free 2-phenylthiophenol, DBT, and biphenyl + H$_2$S are evolved in a relative ratio of 48:42:10. In the presence of an excess of DBT, the reaction is catalytic and converts 10 mol of DBT/mol of **5** in 24 h to both hydrogenation (60%) and desulfurization (40%) products. A rationale of the catalysis cycle is discussed in the light of the results of a study involving the use of isolated compounds in a variety of independent reactions. In accord with previous studies, the thiolate complex **7** is proposed as the intermediate species that undergoes desulfurization by action of H$_2$.

Introduction

Catalytic hydrodesulfurization (HDS) is of prime importance in the petroleum and coal industries because of the growing need to process feedstocks of high sulfur levels with the aim of producing fuels with the smallest possible sulfur content. Residual sulfur in fuels is present mainly in thiophenic forms and predominantly as benzo- and dibenzothiophene derivatives. The mechanisms of HDS of such heteroaromatic compounds has been a subject of continuing discussion over the years, since the understanding of the reaction pathways followed by these molecules is essential for the development of improved practical catalysts.[2]

Homogeneous modeling of the HDS reaction through the study of the coordination and reactivity of thiophenes on metal complexes has emerged as a powerful tool to help elucidate the main mechanistic pathways involved in this important heterogeneous process.[3] Although related studies have provided a wealth of information on the activation and HDS-related reactions of thiophene (T)[3–5] and benzo[*b*]thiophene (BT)[3,6] on transition metal complexes, much less is known about dibenzothiophene (DBT).[3] The latter is a particularly interesting substrate, since it represents a class of compounds present in heavy oils and distillates, which are among the most difficult to desulfurize.[2]

Several bonding modes of T and BT, as well as reactions leading to C–S bond cleavage, hydrogenation, and desulfurization, have been described in detail.[3–6] On the other hand, DBT has been much less studied. Coordination to metals through the sulfur atom (η^1-*S*)[7–12] or through one[10,13–15] or both[14,15] of the benzene rings (η^6) has been demonstrated in several cases; little

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is known, however, about the reactivity of coordinated DBT. There is one example by Jones and Dong[16] of C−H and C−S activation by Rh to yield, respectively, the DBTyl complex $(C_5Me_5)Rh(PMe_3)H(SC_{12}H_7)$ and the ring-opened derivative $(C_5Me_5)Rh(PMe_3)(SC_{12}H_8)$; a recent report by Garcia and Maitlis[17] describes the insertion of Pt(0) to the C−S bond of DBT to yield the thia metallocycle $Pt(SC_{12}H_8)(PEt_3)_2$ which could be cleaved with protonic as well as hydridic reagents to yield free 2-phenylthiophenol and biphenyl, respectively.

Following our previous reports on HDS-related chemistry of T[4] and BT[6] promoted by Ir−triphos complexes [triphos = $MeC(CH_2PPh_2)_3$], in this paper we describe C−H and C−S activation reactions of DBT by the [(triphos)IrH] fragment leading to (triphos)$Ir(H)_2$(DBTyl) (DBTyl = dibenzothienyl) and (triphos)IrH(η^2-*C,S*-DBT), respectively; the selectivity for one or the other of these processes may be tuned by adjusting the reaction temperature. By treating the complex containing a ring-opened DBT with H_2 under appropriate reaction conditions, we have achieved the unprecedented *homogeneous catalytic HDS of DBT* to yield 2-phenylthiophenol and biphenyl + H_2S, which are the same primary products observed for the *heterogeneous* HDS of DBT;[2,18] furthermore, on the basis of independent reactions performed on isolated complexes, we have been able to identify a number of species and elementary steps involved in the hydrogenation and hydrodesulfurization reactions which allowed us to deduce an overall catalytic cycle for this important transformation. The chemistry herein described constitutes an excellent homogeneous model for one of the most commonly invoked mechanisms for HDS of DBT on solid catalysts.[18]

Experimental Section

General Procedure. All reactions and manipulations were routinely performed under a nitrogen atmosphere by using standard Schlenk techniques unless otherwise stated. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from $LiAlH_4$, CH_2Cl_2 was distilled from CaH_2, and *n*-heptane was distilled from sodium. The solvents were stored over 4-Å molecular sieves and purged with nitrogen before use. Commerical benzo[*b*]thiophene and dibenzothiophene were sublimed prior to use. $HBF_4{\cdot}Et_2O$ (85% solution in Et_2O), CF_3SO_3D (98 atom % D), *n*-butyllithium (1.6 M solution in hexanes), *tert*-butyllithium (1.7 M solution in pentane), and $LiHBEt_3$ (1.0 M solution in THF) were purchased from Aldrich. 2-Phenylthiophenol was prepared following a literature method.[19] All other chemicals were commercial products and used as received without further purification. Literature methods were used for the preparation of (triphos)$Ir(H)_2(C_2H_5)$,[20] (triphos)$Ir(H)_3$,[21] [(triphos)$Ir(H)_2$(THF)]BPh_4,[22] and (triphos)$Ir(H)_2Cl$.[4] All metal complexes were collected on sintered glass frits and washed with appropriate solvents before being dried in a stream of nitrogen. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FT-IR spectrophotometer using samples mulled in Nujol between KBr plates. Deuterated solvents for NMR measurements were dried over molecular sieves. ^1H NMR spectra were obtained on a Bruker ACP 200 (200.13 MHz) spectrometer. ^1H NMR shifts are recorded relative to residual ^1H resonance in the deuterated solvent: CD_2Cl_2, δ 5.32; $CDCl_3$, δ 7.23. The $^{13}C[^1H]$ NMR spectra were recorded on the Bruker ACP 200 instrument operating at 50.32 MHz. The $^{13}C[^1H]$ NMR shifts are given relative to the solvent resonance: CD_2Cl_2, δ 54.2; $CDCl_3$, δ 77.7. $^{31}P[^1H]$ NMR spectra were recorded on either a Varian VXR 300 or a Bruker ACP 200 spectrometer operating at 121.42 and 81.01 MHz, respectively. Chemical shifts are relative to external 85% H_3PO_4 with downfield values reported as positive. Broad band and selective $^1H[^{31}P]$ NMR experiments were carried out on the Bruker ACP 200 instrument equipped with a 5-mm inverse probe and a BFX-5 amplifier device. ^{13}C-DEPT, ^1H, ^{13}C 2D-HETCOR, and $^1H,^1H$ 2D-COSY NMR experiments were conducted on the Bruker ACP 200 spectrometer. Conductivities were measured with an Orion Model 990101 conductance cell connected to a Model 101 conductivity meter. The conductivity data were obtained at sample concentrations of ca. 10^{-3} M in nitroethane solutions at room temperature. GC analyses were performed on a Shimadzu GC-14 A gas chromatograph equipped with a flame ionization detector and a 30-m (0.25-mm i.d., 0.25-μm FT) SPB-1 Supelco fused silica capillary column. GC/MS analyses were performed on a Shimadzu QP 2000 apparatus equipped with a column identical to that used for GC analyses. Reactions at high temperature or under controlled pressure of hydrogen were performed with a Parr 4565 reactor (100 mL) equipped with a Parr 4842 temperature and pressure controller.

Reaction of (Triphos)$Ir(H)_2(C_2H_5)$ (1) with DBT. NMR Experiment. A. 70 °C. A solution of (triphos)$Ir(H)_2(C_2H_5)$ (**1**) (10 mg, 0.012 mmol) and DBT (13 mg, 0.071 mmol) in THF-d_8 (1 mL) was transferred under nitrogen into a 5-mm NMR tube, which was flame sealed and then introduced into a NMR probe preheated at a fixed temperature. The reaction occurred at ca. 70 °C and was followed by $^{31}P[^1H]$ NMR spectroscopy by determining the concentration of **1** and the other products as a function of time. Spectra (acquisition time 15 min) were recorded every 30 s during the first 2 h and then every 30 min for a further 14 h. After the first 30 min, three products were formed in a ratio of 28:40:32. These products were identified (*vide infra*) as arene C−H bond activation products of formulas (triphos)$Ir(H)_2$(2-DBTyl) (**2**), (triphos)$Ir(H)_2$(3-DBTyl) (**3**), and (triphos)$Ir(H)_2$(4-DBTyl) (**4**), respectively. The site of C−H activation in **2** and **3** could not be determined experimentally. The proposed structural assignment is essentially based on indirect evidence (*vide infra*). In contrast, the structure of **4** was unambiguously determined by labeling studies (see below). Conversion > 90% was achieved after ca. 11 h with the following product distribution: **2** (21%), **3** (40%), and **4** (39%). After ca. 16 h (quantitative conversion), these products were detected in a ratio of 18:38:42, respectively.

B. 100 °C. By working as above at 100 °C, a conversion > 90% was reached after ca. 2 h with the following product distribution: **2** (18%), **3** (40%), and **4** (42%). At the quantitative conversion (ca. 3 h), **2**−**4** were detected in a ratio of 10:

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39:51. Upon heating the NMR tube at 100 °C for a further ca. 2 h, **2** and **3** were quantitatively converted to **4**.

C. 120 °C. A 5-mm NMR tube was charged with a mixture of **1** (10 mg, 0.012 mmol) and DBT (13 mg, 0.071 mmol) in THF-d_8 (1 mL) under nitrogen, flame sealed, and kept at 120 °C (oil bath). After ca. 2 h, the tube was cooled to room temperature. The ^1H and ^{31}P [^1H] NMR spectra of this sample showed that the C−S bond cleavage product (triphos)IrH(η^2-*C,S*-DBT) (**5**) (see below) formed along with the C−H activation products with the following product distribution: **2** (4%), **3** (8%), **4** (80%), and **5** (8%). After 3 h, the products were present in a ratio of 2:6:72:20.

D. 160 °C. When the reaction was performed as above at 160 °C for 4 h, **5** was the only product detected in solution. For periods less than 4 h, variable amounts of **2**−**4** were also present in the reaction mixture.

Synthesis of (Triphos)Ir(H)$_2$(4-DBTyl) (4). A Parr reactor was charged with a solid sample of **1** (0.25 g, 0.30 mmol) and a solution of DBT (0.33 g, 1.80 mmol) in THF (50 mL) under nitrogen at room temperature and then heated at 100 °C. After 5 h, the bomb was cooled to room temperature and the contents were transferred into a Schlenk-type flask. Portionwise addition of *n*-heptane (40 mL) led to the precipitation of **4** as off-white microcrystals, which were collected by filtration and washed with diethyl ether; yield 85%. When the reaction was carried out for periods less than 5 h, variable amounts of **2** and **3** were detected in the reaction mixture. Compounds **2**−**4** are stable in solvents such as THF and acetone up to 60−70 °C. At higher temperatures (up to ca. 120 °C), the isomerization process of **2** and **3** to **4** is accompanied by some decomposition unless excess DBT is present in solution.

Compound 2. IR: ν(Ir-H) 2070 (s) cm^{-1}. ^{31}P [^1H] NMR (CD_2Cl_2, 20 °C, AM_2 spin system): −9.9 (P_A), −18.9 (P_v, $^2J(P_AP_M) = 15.0$ Hz). ^1H NMR (CD_2Cl_2, 20 °C): δ 2.8−2.2 [CH_2 (triphos)], 1.54 [q, CH_3 (triphos)], −8.76 (second-order double of multiplets, AA′XX′Y spin system, $|^2J(HP_M) + {}^2J(HP_{M'})| = 124.0$ Hz, $^2J(HP_A) = 14.0$ Hz, IrH).

Compound 3. IR: ν(Ir-H) 2070 (s) cm^{-1}. ^{31}P [^1H] NMR (CD_2Cl_2, 20 °C, AM_2 spin system): −10.0 (P_A), −18.7 (P_M, $^2J(P_AP_M) = 15.0$ Hz). ^1H NMR (CD_2Cl_2, 20 °C): δ 2.8−2.2 [CH_2 (triphos)] 1.55 [q, CH_3 (triphos)], −8.81 (second-order doublet of multiplets, AA′XX′Y spin system, $|^2J(HP_M) + {}^2J(HP_{M'})| = 123.0$ Hz, $^2J(HP_A) = 13.9$ Hz, IrH).

Compound 4. Anal. Calcd (found) for $C_{53}H_{48}IrP_3S$: C, 63.52 (63.01); H, 4.83 (4.73); Ir, 19.18 (19.06); S, 3.20 (3.09). IR: ν(Ir-H) 2070 (s) cm^{-1}. ^{31}P[^1H] NMR (CD_2Cl_2, 20 °C, AM_2 spin system): δ −11.3 (P_A), −18.7 (P_M, $^2J(P_AP_M) = 15.3$ Hz). ^1H NMR (CD_2Cl_2, 20 °C): δ 2.8−2.2 [CH_2 (triphos)], 1.59 [q, CH_3 (triphos)], −8.55, (second-order doublet of multiplets, AA′XX′Y spin system, $|^2J(HP_M) + {}^2J(HP_{M'})| = 120.1$ Hz, $^2J(HP_A) = 12.8$ Hz, IrH). ^{13}C [^1H] NMR (CD_2Cl_2, 20 °C): δ 158.9 (br s, IrC), the other resonances of DBT were masked by those of the phenyl carbons of triphos ligand (120−140 ppm).

Reaction of (Triphos)Ir(H)$_2$Cl with (*n*-Butyllithium + DBT). *n*-Butyllithium (30.5 mL, 48.8 mmol, 1.6 M solution in hexanes) was added to a stirred solution of DBT (5.0 g, 27.2 mmol) in Et_2O (40 mL) at 0 °C over 15 min. The mixture was refluxed for 18 h and cooled to room temperature.[23] A sample of this solution (0.10 mL, 0.039 mmol, 0.388 M) was syringed into a solution of (triphos)Ir(H)$_2$Cl (20 mg, 0.02 mmol) in THF-d_8 (1 mL) at room temperature. The reaction mixture was transferred into a 5-mm NMR tube. The ^{31}P [^1H] NMR spectrum of this sample showed the quantitative formation of **2**−**4** in ca. 28:41:31 ratio.

Reaction of [(Triphos)Ir(H)$_2$Cl + *tert*-Butyllithium] with DBT. *tert*-Butyllithium (0.13 mL, 0.22 mmol, 1.7 M solution in pentane) was syringed into a stirred solution of (triphos)Ir(H)$_2$Cl (0.20 g, 0.20 mmol) in THF (50 mL) at 0 °C. An immediate reaction took place. Gas evolution accompanied by color change from pale yellow to red occurred. Solid DBT (0.23 g, 1.2 mmol) was then added to the reaction mixture. After ca. 10 min, the solution was allowed to reach room temperature, stirred for 2 h, and then concentrated to dryness under vacuum. The ^{31}P [^1H] NMR spectrum of the residue showed the quantitative formation of **2**−**4** in almost the same ratio as above.

Reaction of 4 with HBF$_4$·Et$_2$O. A stoichiometric amount of neat HBF$_4$·Et$_2$O (ca. 70 μL) was syringed into a solution of **4** (0.30 g, 0.30 mmol) in CH_2Cl_2 (30 mL) at room temperature. After 30 min, a solution of $NaBPh_4$ (0.14 g, 0.40 mmol) in ethanol (5 mL) followed by *n*-heptane (30 mL) was added to the reaction mixture. On partial concentration under a brisk flow of nitrogen, off-white crystals of [(triphos)Ir(H)$_2$(η^1-*S*-DBT)]BPh_4 (**6**) (see below) precipitated in 75% yield.

Independent Synthesis of [(Triphos)Ir(H)$_2$(η^1-*S*-DBT)]BPh_4 (6). A solid sample of [(triphos)Ir(H)$_2$(THF)]BPh_4 (0.20 g, 0.16 mmol) was dissolved into a solution of DBT (0.29 g, 1.6 mmol) in CH_2Cl_2 (20 mL). After ca. 15 min, ethanol (10 mL) and *n*-heptane (20 mL) were added to the reaction mixture. Partial evaporation of the solvents under a steady stream of nitrogen led to the precipitation of **6** as an off-white microcrystalline solid in 90% yield. Anal. Calcd (found) for $C_{77}H_{69}BIrP_3S$: C, 69.94 (69.21); H, 5.26 (5.11); Ir, 14.54 (14.00); S, 2.42 (2.23). Λ_M: 49 Ω^{-1} cm^2 mol^{-1}. IR: ν(Ir-H) 2092 (s) cm^{-1}. ^{31}P [^1H] NMR (CD_2Cl_2, 20 °C, AM_2 spin system): δ −1.8 (P_A) −17.0 (P_M, $^2J(P_AP_M) = 16.0$ Hz). ^1H NMR (CD_2Cl_2, 20 °C): δ 2.7−2.3 [CH_2 (triphos)], 1.68 [q, CH_3 (triphos)], −9.46 (second-order doublet of multiplets, AA′XX′Y spin system, $|^2J(HP_M) + {}^2J(HP_{M'})| = 113.3$ Hz, $^2J(HP_A) = 10.7$ Hz, IrH).

Reaction of 6 with CO. Carbon monoxide was bubbled through a CH_2Cl_2 (20 mL) solution of **6** (0.20 g, 0.15 mmol) at room temperature for 2 h. After the solvent was removed under vacuum, a pale yellow solid was obtained which was characterized by IR and NMR spectroscopy as a 1:1 mixture of DBT and [(triphos)Ir(H)$_2$(CO)]BPh_4.[21]

Reaction of 4 with CF_3SO_3D under CO. A stoichiometric amount of neat CF_3SO_3D (ca. 25 μL) was syringed into a solution of **4** (0.30 g, 0.30 mmol) in CH_2Cl_2 (30 mL) under CO atmosphere at room temperature. After 3 h, the solution was concentrated to dryness in vacuo. ^1H and ^{31}P NMR spectra of a portion of the residue showed the quantitative conversion of **4** to [(triphos)Ir(H)$_2$(CO)](CF_3SO_3). The rest of the residue was chromatographed on a silica gel column with *n*-pentane as eluant. The eluate was concentrated to dryness and dissolved in CD_2Cl_2. The ^1H NMR spectrum of this sample showed that deuterium was incorporated exclusively in the 4-position of DBT. This was established by integrating the individual DBT peaks.[24] This finding confirmed the structure assigned to **4** where the DBTyl ligand binds iridium *via* the C_4 carbon atom.

Thermal Behavior of 4. A. At 120−160 °C in THF. A 5-mm NMR tube was charged with a THF-d_8 (0.7 mL) solution of **4** (30 mg, 0.03 mmol) under nitrogen, flame sealed, and kept at 120 °C (oil bath). After 3 h, the tube was cooled to room temperature. ^1H and ^{31}P [^1H] NMR spectra of this sample showed the partial conversion of **4** to both **5** (ca. 10%) and several unidentified triphos−iridium complexes (ca. 50%) (see text). Free DBT (^1H NMR resonances in the range 7.5−8.4 ppm) was also produced in concentration comparable with that of the unidentified iridium complexes. Analogous behavior was observed at reaction temperatures ranging from 120 to 160 °C. As an example, at 160 °C **5** was produced in ca. 25% yield whereas the extent of decomposition was ca. 70%.

B. At 70−100 °C in Benzene. A solution of **4** (0.10 g, 0.10 mmol) in benzene (30 mL) was heated at 100 °C in a Parr

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reactor. After 1 h, the bomb was cooled to room temperature, the contents were transferred into a Schlenk-type flask, and the volatiles were removed under vacuum. The residue was characterized by ^1H and ^{31}P [^1H] NMR spectroscopy as a 2:3 mixture of **4** and (triphos)Ir$(H)_2(C_6H_5)$.[25] Quantitative formation of free DBT also occurred during the reaction. Further heating for 2 h led to the complete conversion of **4** to the phenyl dihydride complex and free DBT (^1H NMR and GC/MS). Though at a much lower rate, the reaction occurred already at 70 °C.

C. At 160 °C in THF in the Presence of BT. A 5-mm NMR tube was charged with a THF-d_8 (0.7 mL) solution of **4** (30 mg, 0.03 mmol) and a 10-fold excess of BT (40 mg, 0.30 mmol) under nitrogen, flame sealed, and heated to 160 °C (oil bath). After 3 h, it was cooled to room temperature and placed into an NMR spectrophotometer. The ^1H and ^{31}P [^1H] NMR spectra of this sample showed the quantitative conversion of **4** to the 2-vinylthiophenolate complex (triphos)Ir(η^3-S(C_6H_4)-CH=CH_2)[6] and DBT (^1H NMR and GC/MS).

D. At 160 °C in THF in the Presence of DBT. The reaction was worked up as above with **4** (30 mg, 0.03 mmol) and a 10-fold excess of DBT (55 mg, 0.30 mmol) and gave quantitative conversion of **4** to **5**.

Synthesis of (Triphos)IrH(η^2-*C,S*-DBT) (5). A Parr reactor was charged with solid (triphos)Ir$(H)_2(C_2H_5)$ (**1**) (0.25 g, 0.30 mmol) and a solution of DBT (0.33 g, 1.80 mmol) in THF (40 mL) under nitrogen at room temperature and then heated at 160 °C. After 4 h, the bomb was cooled to room temperature and the contents were transferred into a Schlenk-type flask. Addition of *n*-heptane (30 mL) led to the precipitation of **5** as off-white microcrystals, which were collected by filtration and washed with diethyl ether; yield 85%. Anal. Calcd (found) for $C_{53}H_{48}IrP_3S$: C, 63.52 (62.86); H, 4.83 (4.79); Ir, 19.18 (19.00); S, 3.20 (3.06). IR: ν(Ir-H) 2098 (s) cm^{-1}. ^{31}P [^1H] NMR (CD_2Cl_2, 20 °C, AMQ spin system): δ −10.6 (P_A), −23.1 (P_M), −47.0 (P_Q, $^2J(P_AP_M)$ = 13.5 Hz, $^2J(P_AP_Q)$ = 14.4 Hz, $^2J(P_MP_Q)$ = 16.6 Hz). ^1H NMR (CD_2Cl_2, 20 °C): δ 2.7−2.1 [CH_2 (triphos)], 1.45 [q, CH_3 (triphos)], −8.01 (ddd, ^2J(HP) = 153.2, 12.3, 8.8 Hz, IrH). ^{13}C [^1H] NMR (CD_2Cl_2, 20 °C): δ 161.1 (br s, IrC), the other resonances of DBT were masked by those of the phenyl carbons of triphos (120−140 ppm).

Thermal Behavior of 5. A. At 170 °C in THF. A 5-mm NMR tube was charged with a THF-d_8 (0.7 mL) solution of **5** (30 mg, 0.03 mmol) under nitrogen, flame sealed, and kept at 170 °C (oil bath). After 3 h, the tube was cooled to room temperature. The ^1H and ^{31}P [^1H] NMR spectra of this sample showed the partial decomposition of **5** to the same unidentified triphos−iridium compounds (ca. 10%), and the formation of free DBT in a comparable amount (^1H NMR and GC/MS).

B. At 170 °C in THF in the Presence of BT. A 5-mm NMR tube was charged with a THF-d_8 (0.7 mL) solution of **5** (30 mg, 0.03 mmol) and a 10-fold excess of BT (40 mg, 0.30 mmol) under nitrogen, flame sealed, and heated to 170 °C (oil bath). After 3 h, the tube was cooled to room temperature and placed into an NMR spectrophotometer. The ^1H and ^{31}P [^1H] NMR spectra of this sample showed the partial conversion of **5** to (triphos)Ir(η^3-S(C_6H_4)CH=CH_2)[6] and DBT (43%).

Reaction of 5 with H_2. A. 100 °C, 5 atm; Synthesis of (Triphos)Ir$(H)_2(SC_{12}H_9)$ (7). A solution of **5** (0.25 g, 0.25 mmol) in THF (30 mL) was pressurized with hydrogen to 5 atm at room temperature in a Parr reactor and then heated at 100 °C for 4 h. The bomb was then cooled to room temperature, and after it was depressurized and vented under a nitrogen stream, the contents were transferred into a Schlenk-type flask. Addition of ethanol (30 mL) followed by partial evaporation of the solvents led to the precipitation of the 2-phenylthiophenolate dihydride **7** as pale yellow microcrystals. They were filtered off and washed with *n*-pentane; yield 75%. Anal. Calcd (found) for $C_{53}H_{50}IrP_3S$: C, 63.39 (63.06); H, 5.02 (5.01); Ir, 19.14 (19.09); S, 3.19 (3.03). IR: ν(Ir-H) 2046 (s) cm^{-1}. ^{31}P [^1H] NMR (CD_2Cl_2, 20 °C, AM_2 spin system): δ −2.4, (P_A), −25.5 (P_M, $^2J(P_AP_M)$ = 14.1 Hz). ^1H NMR (CD_2Cl_2, 20 °C): δ 2.6−2.2 [CH_2 (triphos)], 1.49 [q, CH_3 (triphos)], −9.22 (second-order doublet of multiplets, AA′XX′Y spin system, $|^2J(HP_M) + {}^2J(HP_{M'})|$ = 132.3 Hz, $^2J(HP_A)$ = 12.2 Hz, IrH).

B. 170 °C, 5 atm. A solution of **5** (0.25 g, 0.25 mmol) in THF (30 mL) was pressurized with hydrogen to 5 atm at room temperature in a Parr reactor and then heated at 170 °C. After 4 h, the bomb was cooled to room temperature. After it was depressurized and vented under a nitrogen stream, the contents were transferred into a Schlenk-type flask. The volatiles were removed in vacuo, and the residue was characterized by ^1H and ^{31}P [^1H] NMR spectroscopy as a 96:4 mixture of **7** and (triphos)Ir$(H)_3$ (**8**).

C. 170 °C, 30 atm. A solution of **5** (0.25 g, 0.25 mmol) in THF (30 mL) was pressurized with hydrogen to 30 atm at room temperature in a Parr reactor and then heated at 170 °C. After 4 h, the bomb was cooled to room temperature and slowly depressurized by bubbling the gaseous phase through an aqueous solution of Pb(II) acetate. H_2S released during the reaction led to the formation of the characteristic black precipitate of PbS, which was authenticated as described in ref 26. The contents of the bomb were then transferred into a Schlenk-type flask. The volatiles were removed in vacuo, and the residue was dissolved in CD_2Cl_2. ^1H and ^{31}P [^1H] NMR spectra of this sample showed the presence of **7** and **8** in a ratio of 31:69. The sample was chromatographed over a silica gel column (5:1 mixture of *n*-pentane/CH_2Cl_2 as eluant) to remove the iridium complexes. The organic phase was evaporated to dryness in vacuo, and the residue, analyzed by ^1H NMR and GC/MS, was found to contain DBT (42%), 2-phenylthiophenol (48%), and biphenyl (10%). Quite similar organic product distribution was found by analyzing the reaction solution, after it was cooled to room temperature, by GC/MS.

2-Phenylthiophenol.[19] ^1H NMR ($CDCl_3$, 20 °C): δ 7.5−7.1 (m, 9H, CH), 3.36 (s, 1H, SH). GC/MS [EIMS, 70 eV, *m/e* (%)]: 186 (70) M^+, 185 (100) $M - H^+$, 152(42) $M - H_2S^+$.

Reaction of 5 with 2-Phenylthiophenol. A solution of **5** (0.25 g, 0.25 mmol) and 2-phenylthiophenol (93 mg, 0.5 mmol) in THF (30 mL) was introduced in a Parr reactor and heated at 170 °C. After 3 h, the bomb was cooled to room temperature. After it was depressurized and vented under a nitrogen stream, the contents were transferred into a Schlenk-type flask. The volatiles were removed in vacuo, and the residue was characterized as a 61:39 mixture of **7** and **5** (^1H and ^{31}P [^1H] NMR). The formation of DBT also occurred during the reaction (^1H NMR and GC/MS).

Reaction of (Triphos)Ir$(H)_3$ (8) with 2-Phenylthiophenol. A. A 5-mm NMR tube was charged with a mixture of (triphos)Ir$(H)_3$ (**8**) (20 mg, 0.025 mmol) and 2-phenylthiophenol (9 mg, 0.05 mmol) in THF-d_8 (0.7 mL) under nitrogen, flame sealed, and kept at 170 °C (oil bath). After 3 h, the tube was cooled to room temperature. The ^1H and ^{31}P [^1H] NMR spectra of this sample indicated the partial conversion of **8** to **7** (31%) and the formation of hydrogen (^1H NMR: singlet at 4.7 ppm).

B. 30 atm of H_2. A solution of **8** (0.20 g, 0.25 mmol) and 2-phenylthiophenol (93 mg, 0.5 mmol) in THF (30 mL) was introduced in a Parr reactor, pressurized with H_2 to 30 atm, and heated at 170 °C. After 3 h, the bomb was cooled to room temperature. After it was depressurized and vented under a nitrogen stream, the contents were transferred into a Schlenk-type flask. The volatiles were removed in vacuo, and the residue was characterized by ^1H and ^{31}P [^1H] NMR and GC/MS as a mixture of **8** (90%) and **7** (10%).

Thermal Behavior of 7. A. A 5-mm NMR tube, charged with a THF-d_8 (0.7 mL) solution of **7** (30 mg, 0.03 mmol) under nitrogen, was flame sealed and heated to 170 °C (oil bath).

(25) Bianchini, C.; Barbaro, P.; Meli, A.; Peruzzini, M.; Vacca, A.; Vizza, F. *Organometallics* **1993**, *12*, 2505.

(26) Koltoff, I. M.; Sandell, E. B. *Textbook of Quantitative Inorganic Analysis*; MacMillan Co.: New York, 1943.

After 14 h, it was cooled to room temperature and placed into an NMR spectrophotometer. the ^1H and ^{31}P [^1H] NMR spectra of this sample indicated the partial conversion of **7** to **5** (18%) and hydrogen evolution (^1H NMR: singlet at 4.7 ppm). Appreciable formation (12%) of unidentified iridium compounds also occurred (see text).

B. In the Presence of DBT. Workup as above starting with **7** (30 mg, 0.03 mmol) and a 10-fold excess of DBT (55 mg, 0.30 mmol) gave the partial conversion of **7** to **5** (46%) and the formation of hydrogen and 2-phenylthiophenol in an amount of ca. 15% based on **7** (^1H NMR and GC/MS).

Reaction of 7 with H_2. A. 170 °C, 5 atm. A solution of **7** (0.25 g, 0.25 mmol) in THF (30 mL) was pressurized with hydrogen to 5 atm at room temperature in a Parr reactor and then heated at 170 °C. After 14 h, the bomb was cooled to room temperature. After it was depressurized and vented under a nitrogen stream, the contents were transferred into a Schlenk-type flask. The volatiles were removed in vacuo, and the residue was characterized by ^1H and ^{31}P [^1H] NMR spectroscopy as a 90:4:6 mixture of **7**, **5**, and **8**. Free DBT was also detected in solution (ca. 5% based on **7**).

B. 170 °C, 30 atm. A solution of **7** (0.25 g, 0.25 mmol) in THF (50 mL) was pressurized with hydrogen to 30 atm at room temperature in a Parr reactor and then heated at 170 °C. After 14 h, the bomb was cooled to room temperature and depressurized by slowly bubbing the gaseous phase through an aqueous solution of Pb(II) acetate. H_2S released during the reaction led to the formation of the characteristic black precipitate of PbS. The contents of the bomb were then transferred into a Schlenk-type flask. The volatiles were removed in vacuo, and the residue was dissolved in CD_2Cl_2. ^1H and ^{31}P [^1H] NMR spectra of this sample showed the presence of **7** and **8** in a ratio of 64:36. The sample was then chromatographed on a silica gel column (5:1 mixture of *n*-pentane/CH_2Cl_2 as eluant) to eliminate the iridium complexes. The eluate was then concentrated to dryness in vacuo, and the residue was characterized by ^1H NMR and GC/MS as a mixture of DBT (2%), 2-phenylthiophenol (57%), and biphenyl (41%).

Synthesis of (Triphos)Ir(H)$_2$SH (9). A Parr reactor was charged with a solid sample of **1** (0.25 g, 0.30 mmol) and a H_2S-saturated THF (40 mL) solution at room temperature and then heated at 70 °C. After 6 h, the bomb was cooled to room temperature and depressurized and the contents were transferred into a Schlenk-type flask. Portionwise addition of *n*-heptane (40 mL) led to the precipitation of **9** as off-white microcrystals, which were collected by filtration and washed with *n*-pentane; yield 80%. Anal. Calcd (found) for $C_{41}H_{42}IrP_3S$: C, 57.80 (57.12); H, 4.97 (4.93); Ir, 22.56 (21.99); S, 3.76 (3.58). IR: ν(Ir-H) 2050 (s) cm^{-1}. ^{31}P [^1H] NMR (CD_2Cl_2, 20 °C, AM_2 spin system): δ −1.0 (P_A), −25.8 (P_M, $^2J(P_AP_M)$ = 14.0 Hz). ^1H NMR (CD_2Cl_2, 20 °C): δ 2.5−2.2 [CH_2 (triphos)], 1.51 [q, CH_3 (triphos)], −2.58 (m, IrSH), −9.28, (second-order doublet of multiplets, AA'XX'Y spin system, $|^2J(HP_M) + {}^2J(HP_{M'})|$ = 134.8 Hz, $^2J(HP_A)$ = 11.3 Hz, IrH).

Reaction of 9 with H_2. A solution of **9** (0.21 g, 0.25 mmol) in THF (50 mL) was pressurized with hydrogen to 30 atm at room temperature in a Parr reactor and then heated at 170 °C. After 14 h, the bomb was cooled to room temperature and depressurized by slowly bubbling the gaseous phase through an aqueous solution of Pb(II) acetate. H_2S released during the reaction led to the formation of the characteristic black precipitate of PbS. The contents of the bomb were then transferred into a Schlenk-type flask. The volatiles were removed in vacuo, and the residue was dissolved in CD_2Cl_2. ^1H and ^{31}P [^1H] NMR spectra of this sample showed the presence of **9** and **8** in a ratio of 80:20.

Catalytic Hydrogenation and Hydrodesulfurization Reaction of DBT. A solution of **5** (0.20 g, 0.20 mmol) and an 80-fold excess of DBT (0.44 g, 16 mmol) in THF (100 mL) was pressurized at 30 atm at room temperature into the Parr reactor and then heated at 170 °C. After 24 h, the bomb was cooled to room temperature and slowly depressurized by bubbling the gaseous phase through an aqueous solution of Pb(II) acetate. H_2S released during the reaction led to the formation of the characteristic black precipitate of PbS. The contents of the bomb were then transferred into a Schlenk-type flask. The volatiles were removed in vacuo, and the residue was dissolved in CD_2Cl_2. ^1H and ^{31}P [^1H] NMR spectra of this sample showed the presence of **7** and **8** in a ratio of 12:88. The sample was then chromatographed on a silica gel column (5:1 mixture of *n*-pentane/CH_2Cl_2 as eluant) to eliminate the iridium complexes. The eluate was then concentrated to dryness in vacuo, and the residue was characterized by ^1H NMR and GC/MS as a mixture of DBT (87%), 2-phenylthiophenol (8%), and biphenyl (5%). Almost identical conversions and product distribution were observed when an analogous reaction was carried out in the presence of an excess of elemental mercury.[27]

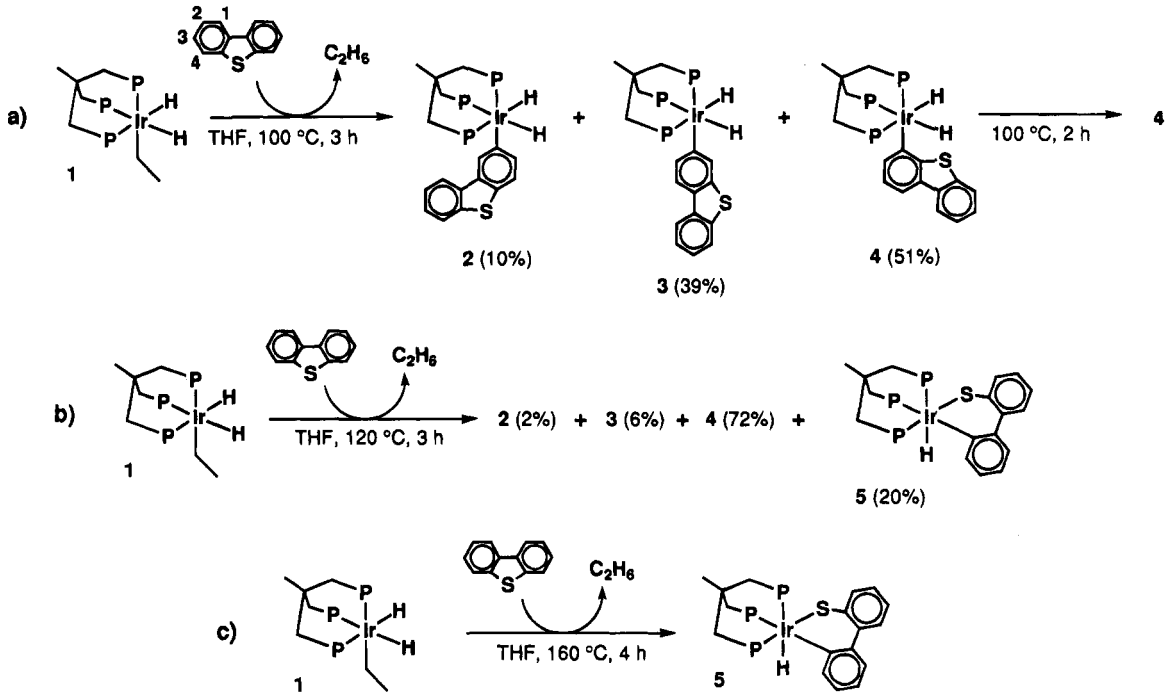
Results and Discussion

The preparations and the principal reactions of the complexes described in this paper are illustrated in Schemes 1−10. Selected IR and NMR spectral data for all products are reported in the Experimental Section. With the exception of the C−S bond cleavage product (triphos)IrH(η^2-*C*,*S*-DBT) (**5**), all the new iridium complexes adopt the same primary coordination geometry. This consists of an octahedral arrangement of six donor atoms about iridium comprising the three phosphorus atoms of a *fac* triphos molecule (^{31}P [^1H] NMR AM_2 pattern), two chemically but not magnetically equivalent terminal hydrides (^1H NMR AA'XX'Y spin system where X, X', and Y are the phosphorus nuclei), and either a carbon or sulfur atom.[20,21,25] All complexes are stereochemically rigid in solution on the NMR time scale and air-stable in both the solid state and solution.

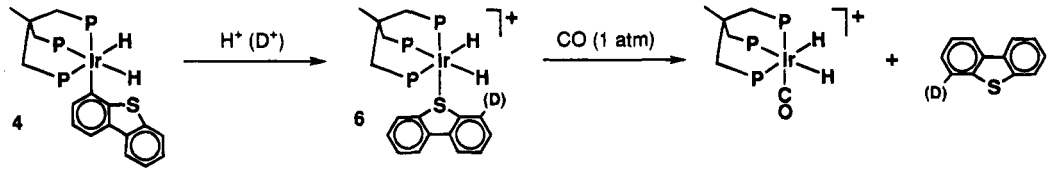
Thermolysis of (Triphos)Ir(H)$_2$(C$_2$H$_5$) (1) in the Presence of DBT in the Temperature Range from 70 to 100 °C. Thermolysis of the ethyl dihydride complex **1** in THF occurs already at 70 °C and produces ethane and the [(triphos)IrH] fragment.[25] In the absence of added substrates, this highly energetic 16-electron metal system activates the solvent to give several unidentified products, due to both primary and secondary insertion of iridium into C−H bonds from THF (for simplicity these products are reported as "decomposition products" in the schemes).[25] However, when the thermolytic reaction is carried out in the presence of a slight excess of DBT, oxidative addition of DBT C−H bonds at iridium prevails over THF activation. In the temperature range from 70 to 100 °C and within 5 h, the C−H bond cleavage is not regioselective as three DBTyl complexes are invariably formed (Scheme 1a). In contrast, after 5 h at 100 °C, a unique product is obtained in quantitative yield. This complex can safely be formulated as (triphos)Ir(H)$_2$(4-DBTyl) (**4**) in the light of the labeling experiment illustrated in Scheme 2. The experiment involves treatment of **4** in CH_2Cl_2 with CF_3SO_3D followed by addition of CO (1 atm) to give free DBT selectively deuterated in the 4 position. Prior to CO addition, an η^1-*S*-DBT adduct of the formula [(triphos)Ir(H)$_2$(η^1-*S*-DBT)]$^+$ can be isolated as the tetraphenylborate salt **6**. The present protonation reaction thus closely resembles that recently reported by Angelici for Cp(PMe$_3$)$_2$Ru(2-

(27) Lin, Y.; Finke, R. G. *Inorg. Chem.* **1994**, *33*, 4891.

Scheme 1



Scheme 2



BTyl) (BTyl = benzothienyl).[28] η^1-*S*-Coordination is quite common for DBT; see, for example, $[Cp(CO)_2Ru(\eta^1\text{-}S\text{-DBT})]BF_4$,[7] $[IrH_2(\eta^1\text{-}S\text{-DBT})(PPh_3)_2]PF_6$,[8] $[Cp(CO)(PPh_3)Ru(\eta^1\text{-}S\text{-DBT})]BF_4$,[9] $Cp^*MCl_2(\eta^1\text{-}S\text{-DBT})$ (M = Rh, Ir),[10] $[Fe(\eta^1\text{-}S\text{-DBT})(CO)_2(Cp)]BF_4$,[11] and $Cp(CO)_2Re(\eta^1\text{-}S\text{-DBT})$.[12]

The structure of the other two DBTyl dihydride complexes, **2** and **3**, obtained at either temperatures below 100 °C or times shorter than 5 h at 100 °C is still ambiguous. Actually, it is possible that **2** may have the structure of **3** and *vice versa*. Our assignment as shown in Scheme 1a is essentially based on reasoning rather than on direct experiments. In no way, in fact, were we capable of preparing pure samples of either **2** or **3** to carry out labeling studies. Neither were helpful for structural assignments of the reactions of (triphos)Ir(H)$_2$Cl with (*n*-BuLi + DBT) or *t*-BuLi/DBT carried out at room temperature. In both cases, mixtures of **2**–**4** were invariably obtained. On the other hand, from a perusal of the variable-temperature thermolysis reactions as well as the metathetical and dehydrohalogenation[29] reactions of (triphos)Ir(H)$_2$Cl, one may draw out the following conclusions. (i) The barriers to insertion of iridium into the C_4–H, C_3–H, and C_2–H bonds of DBT are quite comparable in energy. (ii) The thermodynamic stability of the C–H bond cleavage products follows the order **4** > **3** > **2**. Just on the basis of this stability trend, compound **3** is suggested to contain a 3-DBTyl ligand as it is less sterically demanding than the 2-DBTyl one.

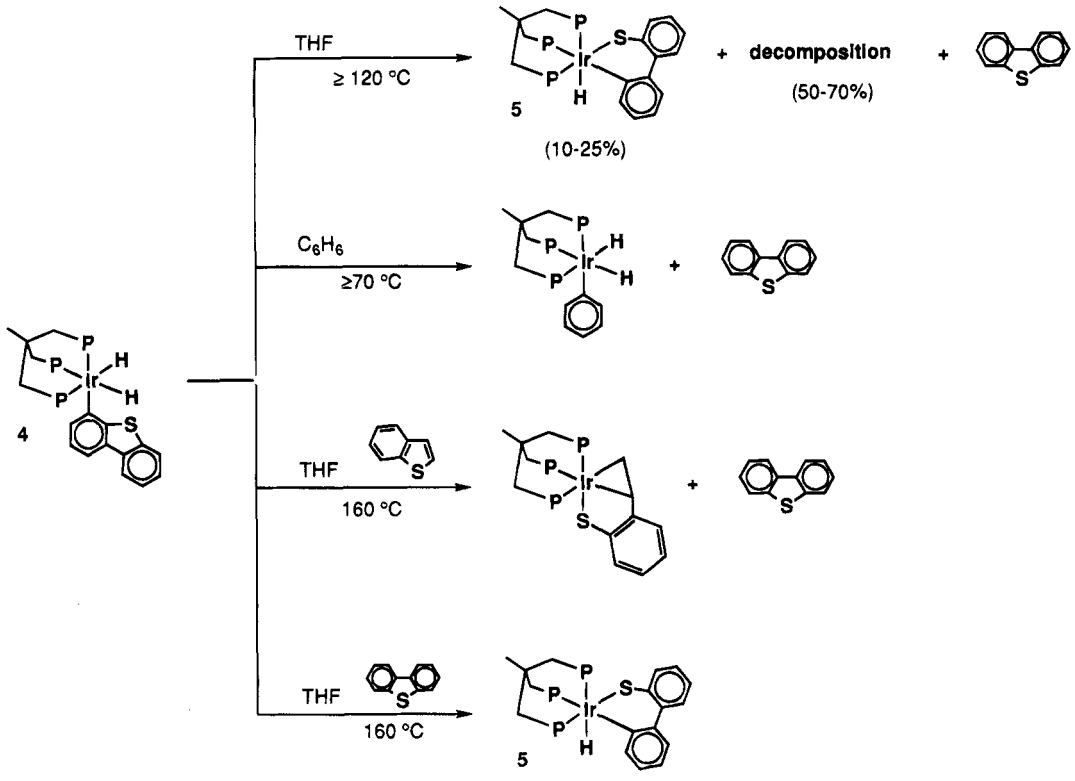
The greater stability of the 4-DBTyl isomer is not surprising in view of previous reports according to which metalation of DBT by RLi or RK compounds, followed by carbonation or bromination, affords DBTs substituted at the 4 position.[23] Metalation of DBT at the 3 position is also possible with the use of phenylcalcium iodide,[23c] while the direct substitution in the 2 position may be achieved *via* electrophilic attack.[30] There is no method for the direct introduction of substituents into the 1 position.[23c] In general, however, substitution reactions *via* metalation exhibit low yields (30–50% in the 4-substituted product), which suggests that the metalation reactions are not regioselective and that the isolation of the 4-substituted products is just due to the greater reactivity of metalated 4-DBTyl compounds toward electrophilic substitution. Indeed, we have the same evidence: the metalation reaction of DBT by [(triphos)IrH] is not regioselective, and the 4-DBTyl derivative is the thermodynamically most stable isomer.

DBTyl metal complexes obtained *via* C–H bond activation of DBT are much less numerous than η^1-*S*-DBT complexes. To the best of our knowledge, the only known complex is Jones' compound, $(C_5Me_5)Rh(PMe_3)H(SC_{12}H_7)$, prepared by thermolysis in hexane of $(C_5Me_5)Rh(PMe_3)(Ph)H$ in the presence of DBT.[16]

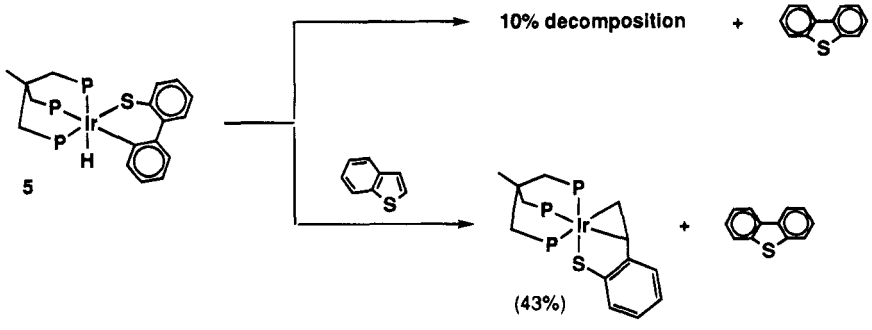
Thermolysis of (Triphos)Ir(H)$_2$(C$_2$H$_5$) (1) in the Presence of DBT at Temperatures Higher than 100 °C. When the thermolysis reaction of **1** in the

(28) Benson, J. W.; Angelici, R. *J. Inorg. Chem.* **1993**, *32*, 1871.
(29) Heyn, R. H.; Caulton, K. G. *J. Am. Chem. Soc.* **1993**, *115*, 3354.
(30) (a) Courtot, P.; Nicolas; Liang, Y. *Compt. Rend.* **1928**, *186*, 1624. (b) Courtot, P.; Pomonis. *Compt. Rend.* **1926**, *182*, 931. (c) Cullinane; Davies; Davies. *J. Chem. Soc.* **1936**, 1435. (d) Courtot, P.; Kelner. *Compt. Rend.* **1934**, *198*, 2003.

Scheme 3



Scheme 4[a]



[a] Reaction conditions: THF, 170 °C, 3 h.

presence of DBT is carried out at temperatures higher than 100 °C, the 4-DBTyl complex becomes the largely predominant product among the C−H bond activation complexes and, more importantly, a new complex begins to form. An appreciable concentration (ca. 20%) of the latter product is observed when the mixture of **1** and DBT in THF is heated to 120 °C for 3 h (Scheme 1b). Selective and quantitative formation of this new species, isolable as off-white crystals, occurs as the reaction mixture is heated to 160 °C for 4 h (Scheme 1c).

Unambiguous identification of the new complex as the C−S insertion product (triphos)IrH(η^2-*C*,*S*-DBT) (**5**) is provided by NMR spectroscopy. ^{1}H NMR examination of the sample in CD_2Cl_2 shows the presence of a unique terminal hydride at −8.01 ppm lying *trans* to a phosphorus atom ($J(HP_{trans})$ = 153.2 Hz) and *cis* to two inequivalent phosphorus nuclei ($J(HP_{cis})$ = 12.3 and 8.8 Hz) (ν(Ir-H) = 2098 cm^{-1}). In accord with the inequivalence of the three phosphorus atoms of triphos, the ^{31}P [^{1}H] NMR spectrum consists of an AMQ spin system. Finally, the insertion of iridium into a C−S bond of DBT is clearly shown by the low-field shift of a DBT carbon resonance which moves to 161.1 ppm (Ir*C*). Indeed, almost identical ^{13}C NMR chemical shifts of the metalated carbon atom have been observed for the other two known examples of metal complexes containing an open DBT molecule: $(C_5Me_5)Rh(PMe_3)(SC_{12}H_8)$ [δ 159.9 (Rh*C*)][16] and $Pt(SC_{12}H_8)(PEt_3)_2$ [δ 158.0 (Pt*C*)].[17]

Thermolysis Reactions of the 4-DBTyl Complex In the Presence of Various Substrates. In an attempt to gain insight into the mechanism of conversion of the C−H bond insertion product **4** to the C−S insertion product **5**, a number of independent thermal reactions have been performed using isolated samples of both complexes (Schemes 3 and 4).

In THF. Heating a sample of **4** in THF at temperatures higher than 120 °C results in formation of **5** in concentrations that increase with temperature but never exceed 25% due to competitive C−H bond activation of the solvent by the [(triphos)IrH] fragment. Free DBT is also formed in an amount corresponding to that of THF activation products.

In C_6H_6. Thermolysis in benzene at 100 °C for 3 h quantitatively transforms **4** into the known phenyl dihydride complex (triphos)Ir(H)$_2$(C_6H_5)[25] and free DBT.

Though at a lower rate, this transformation occurs also at 70 °C.

In THF/BT. Stirring **4** in THF at 160 °C for 3 h in the presence of an excess of BT gives the 2-vinylthiophenolate complex (triphos)Ir(η^3-S(C_6H_4)CH=CH_2)[6] and DBT in quantitative yield.

In THF/DBT. Substitution of DBT for BT in the above reaction leads to quantitative conversion of **4** to **5**.

From these studies it is concluded that the C−H insertion product **4** is not a direct intermediate to the C−S insertion product **5**. As previously noted for similar activation reactions of T[4] and BT[31] at the [(triphos)IrH] system, also the DBTyl and η^2-*C,S*-DBT compounds form in parallel reactions over the temperature range from 120 to 160 °C; at the latter temperature the formation of the thermodynamically more stable C−S insertion product prevails over formation of the C−H cleavage product. Quantitative formation of **5**, however, occurs only when an excess of DBT is added. This suggests that the reductive coupling occurring at **4** is followed by either dissociation of DBT or formation of a labile η^2-*C,C*-DBT intermediate that, before slipping to η^1-*S*-coordination, is displaced by a competing substrate. Indeed, when there is no excess of DBT, other substrates in large concentration (the THF and C_6H_6 solvents or added BT) prevail over DBT for interaction with the [(triphos)IrH] fragment (Scheme 3).

Thermal Behavior of (Triphos)IrH(η^2-*C,S*-DBT). Once formed, the C−S insertion product **5** is thermally stable in THF up to 160 °C. This behavior apparently differs from that of the analogous thiophene (T) and benzo[*b*]thiophene (BT) derivatives (triphos)IrH(η^2-*C,S*-T)[4] and (triphos)IrH(η^2-*C,S*-BT)[6] which thermally undergo the reductive coupling of the terminal hydride with the vinyl moiety of the cleaved T and BT ligands. As a result, η^3-*C,C,S*-butadienethiolate and η^3-*C,C,S*-2-vinylthiophenolate complexes are formed as thermodynamically stable products. A similar reductive coupling process does occur when **5** is heated in THF at temperatures higher than 100 °C in the presence of a reagent capable of trapping the electronically and coordinatively unsaturated 2-phenylthiophenolate fragment [(triphos)Ir($SC_{12}H_9$)]. Appropriate trapping reagents may be either monodentate ligands such as CO to give (triphos)Ir(CO)($SC_{12}H_9$)[32] or binuclear molecules capable of oxidative addition such as H_2 (*vide infra*).

Above 160 °C in pure THF, **5** starts decomposing to give DBT and the above-mentioned products derived from C−H bond cleavage of the solvent. In comparison with the C−H activation product **4**, the reductive elimination of DBT from the C−S insertion product **5** is thus a process that occurs with a higher energy barrier. At 170 °C, only 10% of the starting complex disappears in 3 h. Under these conditions but in the presence of an excess of BT, the loss of DBT from **5** is faster (43%) and the 2-vinylthiophenolate complex is obtained (Scheme 4).

In view of these results we propose that, above 160 °C, **5** is in equilibrium with an η^1-*S*-DBT species. In the presence of an excess of BT,[33] the intact DBT ligand can be displaced by BT in excess, which is then opened and hydrogenated *via* hydride migration.[6] Hence, what we suggest for DBT is quite consistent with previous reports by Jones and co-workers who have proposed η^1-*S*-coordination of thiophenic molecules as a key step for C−S bond scission at 16-electron metal-d^8 fragments.[34] Interestingly, the overall picture of the interaction of [(triphos)IrH] with DBT closely resembles that recently reported for the reaction with ethene in refluxing THF: the vinyl hydride (triphos)Ir($H)_2$(CH=CH_2) and the thermodynamically more stable π-complex (triphos)IrH-(C_2H_4) form in parallel reactions *via* two different transition states.[25]

Hydrogenation and Hydrodesulfurization Reactions of (Triphos)IrH(η^2-*C,S*-DBT). The C−S insertion product **5** in THF quantitatively transforms into the 2-phenylthiophenolate dihydride complex (triphos)-Ir($H)_2$($SC_{12}H_9$) (**7**) by reaction with H_2 (5 atm) at 100 °C for 4 h. Increasing the temperature to 170 °C while keeping constant the H_2 pressure results in the formation of a 96:4 mixture of **7** and (triphos)Ir($H)_3$ (**8**). Free DBT is also produced most likely by displacement of η^1-DBT by H_2. Finally, both hydrogenation (formation of 2-phenylthiophenol) and hydrodesulfurization (formation of biphenyl + H_2S) of DBT occur when the H_2 pressure is increased to 30 atm (Scheme 5). After 4 h at 170 °C and 30 atm of H_2, all iridium of the starting complex **5** is incorporated into a 31:69 mixture of **7** and **8**, while the "open DBT" ligand is converted to a 10:48:42 mixture of biphenyl (+H_2S), 2-phenylthiophenol, and DBT. Under these conditions but in the presence of an excess of DBT (80 equiv), the reaction is catalytic even though with a low rate. In 24 h, 10 mol of DBT/mol of **5** is consumed to give 2-phenylthiophenol (60%) and biphenyl + H_2S (40%), while all iridium is incorporated into a 12:88 mixture of **7** and **8** (Scheme 6). After 48 h of reaction time, 15 mol of DBT/mol of Ir was consumed showing that the system is not deactivated within this time. Almost identical results were obtained when the reaction was carried out in the presence of excess elemental Hg, which indicates that the reaction is truly homogeneous.[27]

The very slow rate, the occurrence of several equilibria, the formation of several products, and the drastic reaction conditions, taken altogether, did not allow us to carry out a kinetic study of the catalytic hydrogenation and hydrodesulfurization of DBT described above. However, valuable mechanistic information was obtained with the use of isolated compounds in a variety of independent reactions carried out under conditions as close as possible to the catalytic ones.

Thermolysis of the 2-Phenylthiophenolate Dihydride Complex 7. In view of the results illustrated in Schemes 5 and 6, it is very likely that the 2-phenylthiophenolate complex **7** plays an intermediate role in both hydrogenation and hydrodesulfurization of DBT assisted by **5**. We have thus looked at the reactivity of **7** in THF at 170 °C.

In the absence of H_2, 30% of **7** converts in 14 h to the C−S insertion product **5** (18%) and to the products of

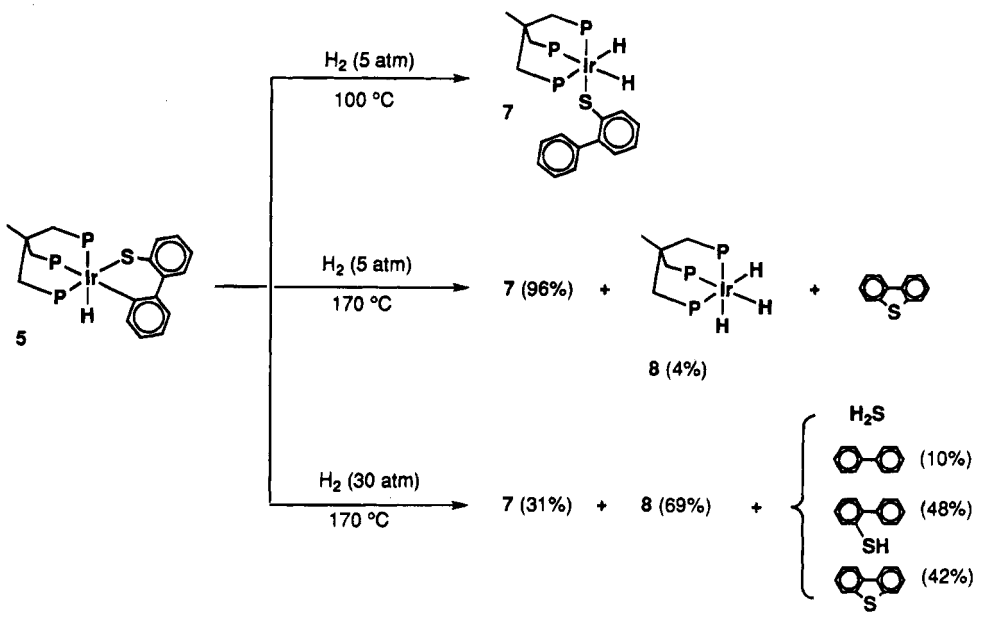
(31) Bianchini, C.; Meli, A. Manuscript in preparation. See also ref 6.

(32) Bianchini, C.; Meli, A. Unpublished results.

(33) An excess of BT is required for the substitution reaction as DBT is a better S-ligand than BT; see refs 7 and 9.

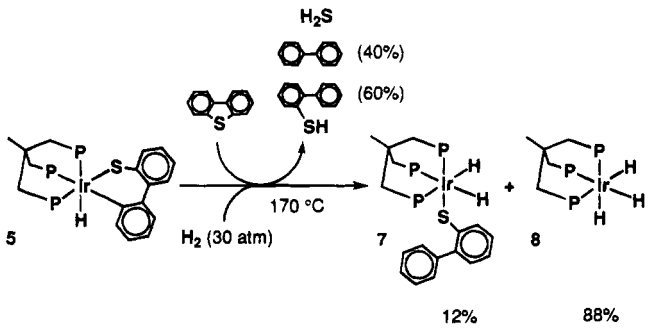
(34) Dong, L.; Duckett, S. B.; Ohman, K. F.; Jones, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 151.

Scheme 5[a]



[a] Reaction conditions: THF, 4 h.

Scheme 6[a]



[a] Conversion: 24 h, 10 mol of DBT/mol of **5**.

C−H bond activation of THF (12%) (Scheme 7a). The concomitant evolution of both H_2 and DBT in comparable amounts rationalizes the thermolysis reaction of **7**. In particular, the formation of H_2 is consistent with the reductive elimination of H_2 from **7** occurring at 170 °C. As a result, the unsaturated fragment [(triphos)-Ir($SC_{12}H_9$)] forms which, in the absence of a trapping reagent (*vide infra*) and at 170 °C, undergoes intramolecualr insertion of iridium into an *ortho* C−H bond of the phenyl ring to give **5**. On the other hand, since the C−S insertion product **5** in THF at 170 °C is in equilibrium with an η^1-*S*-DBT species (reductive ring closure), displacement of DBT by THF can occur to give the unidentified C−H activation products. This reaction path is totally suppressed when the thermolysis of **7** at 170 °C is carried out in the presence of an excess of DBT. Notably, the latter substrate, besides prevailing over THF (see Schemes 1 and 3), is also capable of aiding the reductive elimination of 2-phenylthiophenol by stabilizing the 16-electron fragment (triphos)IrH (See Schemes 7 and 8). The amount of **5** formed upon thermolysis of **7** at 170 °C in the presence of excess DBT (46%) thus comes from two independent reactions. The major path (31%) involves the reductive elimination of H_2 followed by intramolecular insertion of iridium into a C−H bond of the phenyl substituent. The minor path (15%) involves the reductive elimination of 2-phenylthiophenol from **7** followed by coordination and then opening of a DBT molecule by the [(triphos)IrH] fragment. The complicated thermolysis pattern of **7** in THF at 170 °C is summarized in Scheme 8.

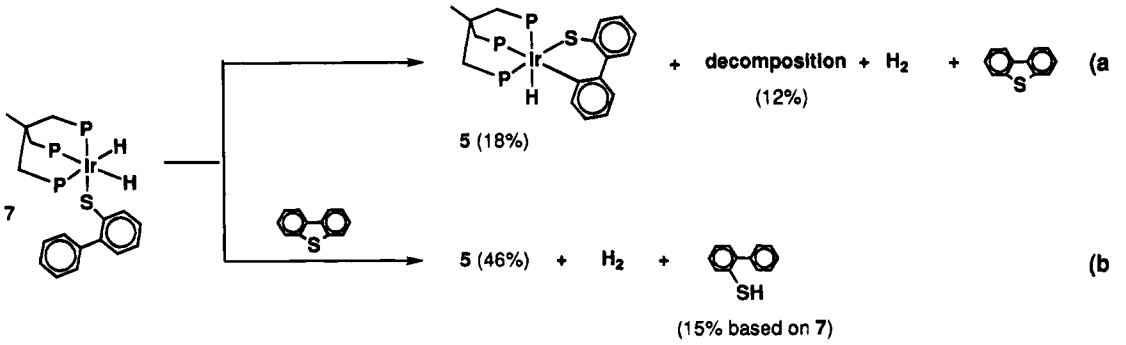
Reactions of the 2-Phenylthiophenolate Dihydride Complex 7 with H_2. Heating a sample of **7** dissolved in THF at 170 °C under 5 atm of H_2 for 4 h results in low conversion of **7** (10%) to **5** (4%), **8** (6%), and free DBT (Scheme 9a). Evidently, the pressure of H_2 slows down the reductive coupling of the two terminal hydrides in **7**. No trace of 2-phenylthiophenol was detected, which confirms the significant role of DBT in promoting the elimination of this thiol from **7**.

The elimination of 2-phenylthiophenol from **7** can also be achieved in the absence of an excess of DBT provided the H_2 pressure is increased to 30 atm (Scheme 9b). In this case, in fact, a larger amount of **7** is converted to **8** (36%), while the 2-phenylthiophenolate ligand is transformed into a 41:57:2 mixture of biphenyl (+H_2S), 2-phenylthiophenol, and DBT. These results are nicely consistent with those reported in Scheme 5 and clearly indicate that **7** can be an important intermediate for both hydrogenation and hydrodesulfurization of DBT at the [(triphos)IrH] fragment.

Reactions of (Triphos)Ir(H)$_3$ (8) with 2-Phenylthiophenol. To our surprise **8** was found to be fully stable when heated in THF at 170 °C in the presence of an excess of DBT. This evidence shows that DBT cannot enter the catalysis cycle *via* **8** and thus suggests that other reaction steps, besides hydrogenation of **7**, are necessary to accomplish the catalytic hydrodesulfurization of DBT.

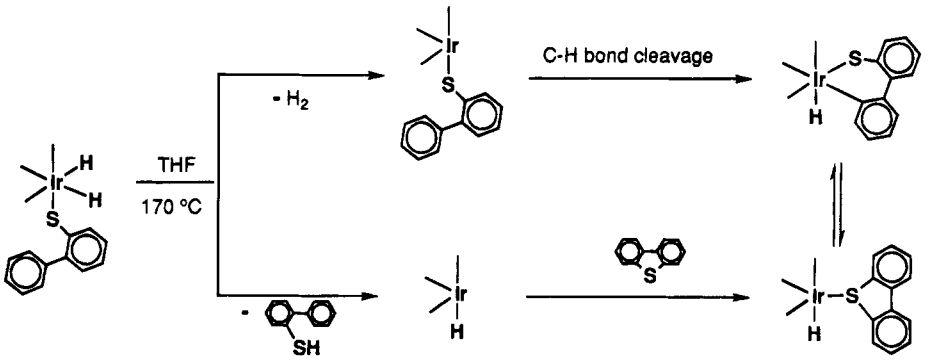
One of these steps may be the reaction of **8** with 2-phenylthiophenol. The trihydride, in fact, reacts in THF at 170 °C with 2-phenylthiophenol to give **7** (31% conversion in 3 h) and H_2. Under a pressure of 30 atm of H_2, though disfavored (10% conversion), this reaction still takes place as it does not proceed *via* thermal elimination of H_2 from **8** followed by S−H oxidative addition. In fact, the trihydride complex is thermally stable in THF at 170 °C, while it is known to react with

Scheme 7[a]

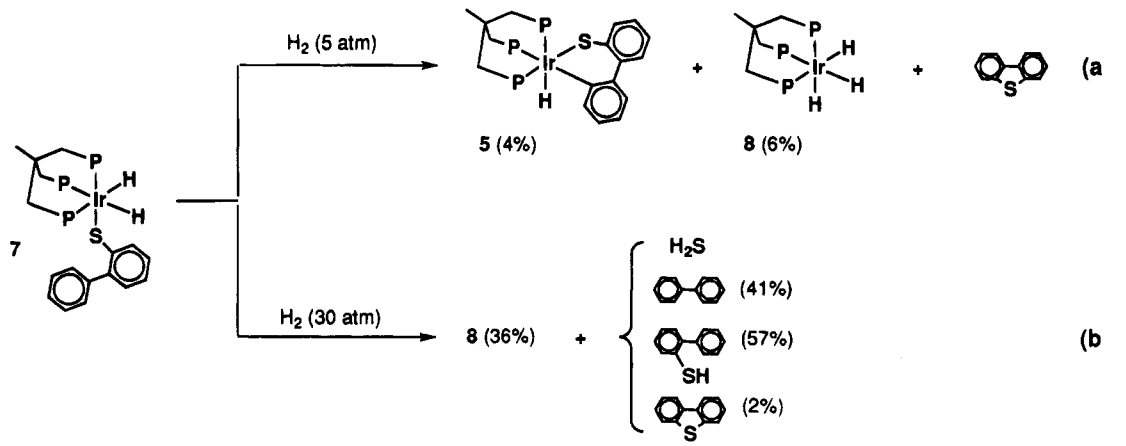


[a] Reaction conditions: THF, 170 °C, 14 h.

Scheme 8



Scheme 9[a]



[a] Reaction conditions: THF, 170 °C, 14 h.

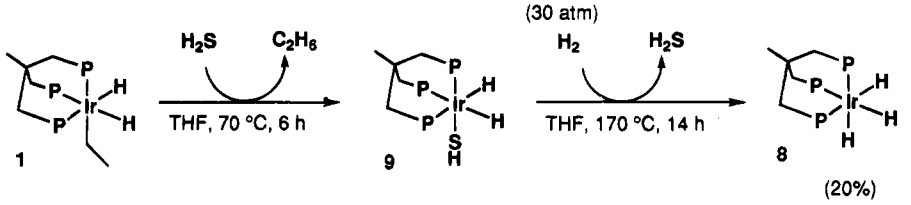
protic acids which generally attack a terminal hydride ligand.[21]

Reaction of (Triphos)IrH(η^2-*C,S*-DBT) (5) with 2-Phenylthiophenol. Having found that 2-phenylthiophenol reacts with **8** under the catalytic conditions, it was of interest to see whether other metal species participating in the catalysis cycle might be attacked by this thiophenol. Indeed, a reaction occurs between the C–S insertion product **5** and a slight excess of 2-phenylthiophenol in THF at 170 °C to give **7** (61% in 3 h) and free DBT. In view of the reactions of 2-phenylthiophenol with **8** and **5**, it is thus conceivable that also the 2-phenylthiophenol produced in the reactions shown in Schemes 5–7 and 9 is actually the result of a mass balance involving several equilibria.

In Search of a Mechanism for the Cleavage of the Ir–S–C Linkage in 7. The reactions of thiols with organometallic compounds have extensively been investigated in recent years. It is generally agreed that (i) metal thiolates are key intermediates in all cases where C–S bond scission is seen, (ii) desulfurization of thiols is aided greatly by the presence of either a hydride source in the reaction mixture or a hydride ligand directly on the complex, and (iii) the C–S bond cleavage occurs *via* migration of a hydride to the sulfur-bound carbon of the thiolate ligand.[35] After the hydrocarbon is eliminated, the remaining M-S moiety may be stabilized by either dimerization (*e.g.*, M(μ-S)$_2$M) or electronic redistribution within the complex (*e.g.*, M=S). In the presence of H_2 as in the case at hand, an M(SH)(H) species may eventually form. In this respect, it is worth mentioning an interesting case of hydrodesulfurization

(35) (a) Wiegand, B. C.; Friend, C. M. *Chem. Rev.* **1992**, *92*, 491 and references therein. (b) Tatsumi, K.; Sekiguchi, Y.; Nakamura, A. *J. Am. Chem. Soc.* **1986**, *108*, 1358. (c) Okasada, K.; Matsumoto, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1985**, *4*, 857.

Scheme 10



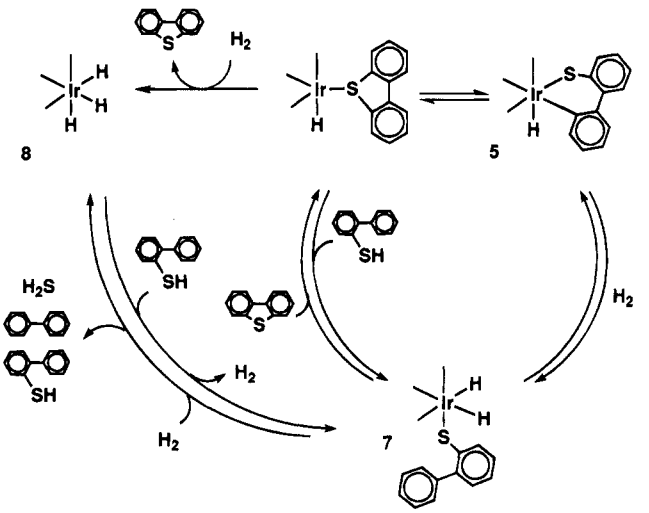
of DBT in homogeneous phase recently reported by Garcia and Maitlis for $Pt(SC_{12}H_8)(PEt_3)_2$.[17] The reaction of the latter complex with Et_3SiH leads to stoichiometric formation of biphenyl and *trans*-$Pt(PEt_3)_2(SH)(H)$, which is converted by HCl to H_2S and *trans*-$Pt(PEt_3)_2(H)(Cl)$.

Intrigued by Maitlis' discovery, we decided to look at the possible intermediacy of (triphos)Ir(SH)$(H)_2$ (**9**) in the hydrogenation of the 2-phenylthiophenolate ligand in **7** (30 atm of H_2, 170 °C). No experimental evidence was obtained for the formation of **9** through a direct study of this reaction on a preparative scale. Then **9** was independently synthesized by thermolysis of **1** in THF at 70 °C in the presence of an excess of H_2S.[36] Interestingly, this mercapto complex in THF does react, even though slowly, with a high pressure of H_2 (>30 atm, 170 °C) to give the trihydride **8** and H_2S (Scheme 10). In light of these precedents and experimental results, it is reasonable to propose that the C−S bond scission step in the HDS of DBT proceeds by reaction of H_2 with complex **7** to yield (triphos)Ir(SH)(H) (**9**) + biphenyl, conceivably via a heterolytic activation, followed by reaction of **9** with H_2 to produce the trihydride **8** + H_2S. However, high-pressure NMR studies would be needed in order to confirm the intermediacy of **9** in the catalytic cycle. In summary, the S−C bond in the Ir-S-$C_{12}H_9$ moiety is cleaved by H_2 to give H_2S and biphenyl, and this reaction occurs at a high pressure of H_2 (>30 atm).

The Catalysis Cycle. Incorporation of all the above experimental evidence leads to the mechanism shown in Scheme 11 for the hydrogenation and hydrodesulfurization of DBT catalyzed by the [(triphos)IrH] fragment. In the scheme, the skeleton of the tripodal ligand and the phosphorus donors are omitted for clarity.

After DBT has been cleaved, the C−S insertion product **5** reacts with H_2 to give the 2-phenylthiophenolate dihydride **7**. This complex has two reaction options: the reductive elimination of 2-phenylthiophenol promoted by interaction with DBT and the further hydrogenation to give 2-phenylthiophenol and biphenyl + H_2S. In the first case, compound **5** is regenerated for use in a following cycle. In the second case, **8** forms and the reaction would stop since the trihydride does not react with DBT. Fortunately, this does not occur as the 2-phenylthiophenol converts **8** to **7** which can reenter the catalysis cycle. Besides the intrinsic kinetic sluggishness of iridium compounds, the low tof of the catalytic reaction seems to be just the slowness with which **8** is converted to **7** by action of 2-phenylthiophenol. In fact, this transformation is disfavored at a high pressure of H_2.

Scheme 11. Proposed Mechanism for the Catalytic Hydrogenation and Hydrodesulfurization of DBT[a]



[a] Reaction conditions: THF, 170 °C, 30 atm of H_2.

Conclusions

The C−S insertion product (triphos)IrH(η^2-*C*,*S*-DBT) (**5**) is the ultimate thermodynamic sink for the system [(triphos)IrH]/DBT. Compound **5** is a catalyst precursor as well as an intermediate species in the homogeneous hydrogenation and hydrodesulfurization of DBT to 2-phenylthiophenol and biphenyl + H_2S. The catalysis reaction, which represents the first example for DBT in homogeneous phase, proceeds *via* several intermediate steps among which is the reaction of **5** with H_2 to give the 2-phenylthiophenolate complex (triphos)Ir$(H)_2$-$(SC_{12}H_9)$ (**7**). Recent reactor and surface studies have provided evidence for a two-stage process involving a metal thiolate in the HDS of DBT.[19,37] This picture thus agrees quite well with that painted by the homogeneous modeling studies presented here. In particular, the present HDS of DBT reasonably accounts for one of the major modes of DBT reactivity on HDS catalysts, namely the direct sulfur extrusion to give biphenyl + H_2S.

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(37) (a) Girgis, M. J.; Gates, B. C. *Ind. Eng. Chem. Res.* **1991**, *30*, 2021 and references therein. (b) Topsøe, H.; Clausen, B. S. *Appl. Catal.* **1986**, *25*, 273. (c) Kasztelan, S. *Langmuir* **1990**, *6*, 590. (d) Brunier, T. M.; Drew, M. G. B.; Mitchell, P. C. H. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 3225.