HDS Model Systems. Coordination, Opening, and Hydrogenation of Benzo[*b*]thiophene at Iridium

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Abstract: The η^4-benzene complexes [(triphos)Ir(C_6H_6)]Y (Y = BPh_4, **1a**; PF_6, **1b**) react with benzo[*b*]thiophene (BT) at room temperature to give the unprecedented [(triphos)Ir(η^3-*C*,*C*,*S*-C_8H_6S)]Y (Y = BPh_4, **2a**; PF_6, **2b**) in which intact BT is coordinated to the metal center through the S atom and the C_2=C_3 bond. **2a** and **2b** are transformed upon mild thermolysis into the iridabenzothiabenzene complexes [(triphos)Ir(η^2-*C*,*S*-C_8H_6S)]Y (Y = BPh_4, **3a**; PF_6, **3b**). An X-ray analysis has been carried out on **3a**·1.5THF·0.5EtOH. The coordination geometry around iridium may be described as a distorted trigonal-bipyramid, the metal center being surrounded by the three phosphorus atoms of triphos and by a carbon and a sulfur atom from a C–S-cleaved BT molecule. Crystal data: triclinic, space group $P\bar{1}$, 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. Interaction of **2a** with CO (1 atm, 20 °C) yields [(triphos)Ir$(CO)_2$]BPh_4 (**4**) plus free BT, whereas **3a** requires more drastic conditions (5 atm, 70 °C) to eliminate BT and produce **4**. **2a** also reacts with H_2 (1 atm, 20 °C) to produce [(triphos)Ir$(H)_2$(η^1-*S*-BT)]BPh_4 (**5**), which can be independently prepared by treatment of [(triphos)Ir$(H)_2$(THF)]BPh_4 with BT; at 5 atm H_2, free BT is obtained together with [(triphos)Ir$(H)_3$], BPh_3, and benzene, as a result of a heterolytic splitting of H_2 at the [(triphos)Ir$(H)_2$]$^+$ fragment assisted by the BPh_4^- counteranion. The C–S-cleaved BT in **3a** is readily hydrogenated (5 atm, 20 °C) to 2-ethylbenzenethiolate, producing [(triphos)Ir$(H)_2${*o*-S-$(C_6H_4)C_2H_5$}] (**8**) plus BPh_3 and benzene also via heterolytic splitting of H_2 assisted by BPh_4^-; protonolysis of **8** with 2 equiv HCl produces (triphos)$IrCl_3$ with concomitant liberation of 2-ethylbenzenethiol, a primary product of BT HDS. If the PF_6^- analogue **3b** is used instead, the reaction with H_2 under identical conditions yields the thiolate-bridged dimer [(triphos)IrH{μ-*o*-S$(C_6H_4)C_2H_5$}$_2$HIr(triphos)]$(PF_6)_2$ (**9b**). **3a** also reacts with $LiHBEt_3$ to give [(triphos)Ir(H)(η^2-*C*,*S*-C_8H_6S)] (**11**), which converts in THF solution at 66 °C into [(triphos)Ir(η^3-S(C_6H_4)-CH=CH_2)] (**12**) by hydride migration to C_2; neither **11** nor **12** react with H_2 under mild conditions. Addition of HBF_4·OEt_2 to **12** yields [(triphos)Ir(η^4-S(C_6H_4)C(H)Me)]BF_4 (**13c**), which does react with H_2 even at 1 atm to give the thiolate-bridged dimer [(triphos)IrH{μ-*o*-S$(C_6H_4)C_2H_5$}$_2$HIr(triphos)]$(BF_4)_2$ (**9c**). **13c** also reacts with H^- to give [(triphos)IrH(η^2-S(C_6H_4)C(H)Me)] (**14**), which in turn reacts with H_2 and HBF_4·OEt_2 to yield **8** and **9c**, respectively.

Introduction

Hydrodesulfurization (HDS) is the process through which sulfur is removed from petroleum and other fossil fuel feedstocks by reaction with hydrogen in order to produce environmentally friendlier fuels. Considering the current world petroleum production, this is probably the largest volume industrial application of transition-metal catalysis. Sulfur in fossil materials is contained in a variety of organic compounds, such as thiols, sulfides, disulfides, and the more refractory thiophenes, benzothiophenes, and dibenzothiophenes; residual sulfur in fuels is found predominantly as benzothiophenes and dibenzothiophenes, which makes these molecules particularly interesting for model studies.[2]

A great deal of attention has been devoted to trying to define the mechanisms of the various steps involved in the HDS reaction of thiophene both on surfaces[3] and on organometallic models.[4] The coordination and reactivity of thiophene (T) on metal complexes has been explored in some detail, but much less is known about the coordination chemistry of benzo[*b*]thiophene (BT).[4]

Concerning the bonding to metal centers, most of the well-characterized complexes known contain BT η^6-coordinated through the benzene ring,[5] but the reactivity resulting from this type of coordination does not appear to parallel HDS-related reactions.[6] η^1-S BT coordination has been demonstrated in several

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cases,[7] as well as an equilibrium between the η^1 and η^2-C=C bonding modes in $Cp(CO)_2Re(BT)$.[7b,c] Also, complexes containing η^1-S and η^2-C=C bonded BT have been suggested as possible intermediates in C–S bond breaking[8] and C=C bond hydrogenation[9,10] reactions. There are no authenticated examples of metal complexes containing BT η^5-bonded through the thiophenic ring, but such species have been proposed as possible intermediates in heterogeneous HDS reactions.[6a] Also, the complex $[(\eta^5\text{-BT})Rh(PPh_3)_2]^+$ has been suggested as an intermediate in the homogeneous catalytic hydrogenation of BT on the basis of the regioselectivity of the catalysis, together with theoretical calculations.[10b,c]

Besides the well-understood homogeneous catalytic hydrogenation of BT to 1,2-dihydrobenzo[*b*]thiophene (DHBT)[9,10] (which does not lead to desulfurized products), little is known about the reactivity of coordinated BT. C–S bond activation leading to ring-opened BT ligands has been reported in a very limited number of cases, *viz.* $Cp^*Rh(PMe)_3(SC_8H_6)$[8] and $(PMe_3)_3Ir(SC_8H_6)Cl$.[11] Only one example of metal-assisted ring 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.[12a] Similarly, $Ru_3(CO)_{12}$ reacts with BT to yield the ring-opened $Ru_2(C_8H_6S)(CO)_6$, analogous to Rauchfuss' benzothiaferrole; thermolysis of this complex leads to sulfur extrusion and production of $Ru_2(C_8H_6)(CO)_6$.[12b]

In this paper we report evidence for an unprecedented mode of BT coordination in $[(triphos)Ir(\eta^3\text{-}C,C,S\text{-}C_8H_6S)]^+$ (**2**). Complex **2** yields the ring-opened derivative $[(triphos)Ir(\eta^2\text{-}C,S\text{-}C_8H_6S)]^+$ (**3**) upon mild thermolysis. The reactivity of **3** toward hydrogen, as well as hydride and proton sources, leads to the production of coordinated 2-ethylbenzenethiolato ligands and ultimately free 2-ethylbenzenethiol, which is one of the primary products of the heterogeneous HDS of BT. These observations provide detailed information at the molecular level, which hopefully will contribute to a better understanding of the various steps involved in the hydrodesulfurization of benzothiophenes. A preliminary communication of part of this work has already appeared.[13]

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) was distilled from $LiAlH_4$ and *n*-heptane from sodium. The solvents were stored over molecular sieves and purged with nitrogen prior to use. Commercial BT (Aldrich) was sublimed prior to use. $LiHBEt_3$ (1.0 M solution in THF), $HBF_4{\cdot}OEt_2$ (85% solution in OEt_2), and BPh_3 were purchased from Aldrich. All other chemicals were commercial products and were used as received without further purification. Literature methods were used for the preparation of $[(triphos)Ir(C_6H_6)]Y$ (Y = BPh_4, **1a**; PF_6, **1b**)[14] and $[(triphos)Ir(H)_2(THF)]BPh_4$ (**7**).[15] 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 either a Bruker ACP 200 (200.13 MHz) or a Bruker AMX 600 (600.14 MHz) spectrometer. ^1H NMR shifts were recorded relative to residual ^1H resonance in the deuterated solvent: CD_2Cl_2, δ 5.32; THF-d_8, δ 3.53 and 1.78. 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 were given relative to the solvent resonance: CD_2Cl_2, δ 54.4; THF-d_8, δ 75.8 and 67.9; acetone-d_6, δ 205.1 and 30.2. $^{31}P\{^1H\}$ NMR spectra were recorded either on 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, 2D-HETCOR, and 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 under controlled pressure of hydrogen or carbon monoxide were performed with a Parr 4565 reactor equipped with a Parr 4842 temperature and pressure controller.

Synthesis of $[(Triphos)Ir(\eta^3\text{-}C,C',S\text{-}C_8H_6S)]BPh_4$ (2a). A solution of **1a** (0.40 g, 0.33 mmol) and BT (1.77 g, 13.18 mmol) in THF (70 mL) was stirred in a thermostated water bath (25 °C) for 5 days. The solution gradually changed its color from yellow orange to red orange. Almost quantitative formation of benzene was detected by GC. After concentration under reduced pressure to ca. 20 mL, the remaining solution was diluted with ethanol (40 mL). On slow concentration under a steady stream of nitrogen, a red orange crystalline precipitate was obtained. This was collected by filtration and washed with ethanol and *n*-pentane. ^1H and $^{31}P\{^1H\}$ NMR spectra showed almost complete conversion (>90%) of **1a** to **2a**. Small amounts (<5%) of the complex $[(triphos)Ir(\eta^2\text{-}C,S\text{-}C_8H_6S)]BPh_4$ (**3a**) (see below) were also detected. Repeated recrystallizations from THF and ethanol gave pure samples of **2a** as brick red crystals in 55% yield. Anal. Calcd (found) for $C_{73}H_{65}BIrP_3S$: C, 69.02 (68.65); H, 5.16 (5.11); Ir, 15.13 (15.01); S, 2.52 (2.35). Λ_M: 55 Ω^{-1} cm^2 mol^{-1}. Higher reaction temperatures accelerate the **1a** to **2a** conversion but also increase the amount of **3a**. Indeed, as shown in an independent reaction, **2a** is stable in ambient-temperature THF solutions, whereas it begins to appreciably convert to **3a** at temperatures higher than 40 °C. As an example, quantitative conversion of 0.2 g of **2a** to **3a** was achieved at reflux temperature in *ca.* 24 h.

Synthesis of $[(Triphos)Ir(\eta^3\text{-}C,C',S\text{-}C_8H_6S)]PF_6$ (2b). This synthesis was carried out analogously to that described for **2a** from **1b** and BT; yield 50%. Anal. Calcd (found) for $C_{49}H_{45}F_6IrP_4S$: C, 53.70 (53.51); H, 4.14 (4.08); Ir, 17.54 (17.33); S, 2.92 (2.81). Λ_M: 76 Ω^{-1} cm^2 mol^{-1}.

Synthesis of $[(Triphos)Ir(\eta^2\text{-}C,S\text{-}C_8H_6S)]BPh_4$ (3a). A solution of **1a** (0.30 g, 0.25 mmol) and BT (0.20 g, 1.50 mmol) in THF (20 mL) was kept at reflux temperature for 20 h during which time the color of the solution changed gradually from yellow orange to orange red. Addition of ethanol (50 mL) and partial evaporation of the solvents under a steady stream of nitrogen led to the precipitation of **3a** as brick red crystals. They were filtered off and washed with ethanol and *n*-pentane; yield 90%. Anal. Calcd (found) for $C_{73}H_{65}BIrP_3S$: C, 69.02 (68.62); H, 5.16 (5.27); Ir, 15.13 (15.00); S, 2.52 (2.38). Λ_M: 56 Ω^{-1} cm^2 mol^{-1}. Well-formed crystals of formula **3a**·1.5THF·0.5EtOH were obtained by slow crystallization of **3a** from THF and ethanol. Anal. Calcd (found) for $C_{80}H_{80}BIrO_2P_3S$: C, 68.56 (68.41); H, 5.75 (5.66); Ir, 13.71 (13.51); S, 2.29 (2.18). Complex **3a** is thermally stable in deaerated common organic solvents (THF, DMSO, MeCN, acetone) are reflux temperature. Also, the complex is air-stable in the solid state, whereas it slowly decomposes in solution.

Synthesis of $[(Triphos)Ir(\eta^2\text{-}C,S\text{-}C_8H_6S)]PF_6$ (3b). This complex was prepared analogously to **3a** from **1b** and BT; yield 80%. Anal. Calcd (found) for $C_{49}H_{45}F_6IrP_4S$: C, 53.70 (53.43); H, 4.14 (4.09); Ir, 17.54 (17.29); S, 2.92 (2.78). Λ_M: 79 Ω^{-1} cm^2 mol^{-1}.

Reaction of 2a with CO. Carbon monoxide was bubbled through a THF (20 mL) solution of **2a** (0.10 g, 0.08 mmol) at room temperature

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for 12 h during which the color of the solution changed from red orange to yellow. After the solvent was removed under vacuum at room temperature, a yellow solid was obtained, which was characterized by IR and NMR spectroscopy as a 1:1 mixture of [(triphos)Ir(CO)$_2$]BPh$_4$[16] (**4**) and BT.

Reaction of 3a with CO. A THF (20 mL) solution of **3a** (0.10 g, 0.08 mmol) was pressurized with CO to 5 atm at 70 °C in a Parr reactor for 2 h. After being depressurized and vented under a nitrogen stream, the contents of the bomb were transferred into a Schlenk-type flask. The volatiles were removed in vacuo at room temperature. The yellow residue was characterized by IR and NMR spectroscopy as a 1:1 mixture of [(triphos)Ir(CO)$_2$]BPh$_4$[16] (**4**) and BT.

Reaction of 2a with Hydrogen. A. 1 atm. Hydrogen was bubbled through a THF (20 mL) solution of **2a** (0.10 g, 0.08 mmol) at room temperature. After 3 h, the reaction mixture was concentrated to dryness in vacuo. Analysis of the residue by IR and NMR spectroscopy showed *ca.* 15% conversion of **2a** to [(triphos)Ir(H)$_2$(η^1-S-BT)]BPh$_4$ (**5**) (see below).

B. 5 atm. A solution of **2a** (0.10 g, 0.08 mmol) and toluene (20 μL, 0.19 mmol, GC internal standard) in THF (20 mL) was pressurized with hydrogen to 5 atm at room temperature in a Parr reactor. After 3 h, the reactor was cooled to 0 °C. After being depressurized and vented under a nitrogen stream, a sample of the solution was withdrawn and analyzed by GC/MS, which showed almost quantitative formation of BT and benzene. The rest of the solution was concentrated to dryness under vacuum, and the residue was found to contain [(triphos)IrH$_3$][17] (**6**) and **5** in a 9:1 ratio (IR and NMR spectroscopy) and triphenylboron (separated by sublimation at 70 °C, 0.5 Torr). The latter product was authenticated (^{1}H NMR) by comparison with an authentic specimen. On further exposure of the residue at 5 atm hydrogen pressure, all **5** converted to **6** and BT.

Independent Synthesis of [(Triphos)Ir(H)$_2$(η^1-S-BT)]BPh$_4$ (5). A solid sample of [(triphos)Ir(H)$_2$(THF)]BPh$_4$ (**7**) (0.20 g, 0.16 mmol) was dissolved into a solution of BT (0.21 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 **5** as an off-white microcrystalline solid in 90% yield. Anal. Calcd (found) for $C_{73}H_{67}BIrP_3S$: C, 68.91 (68.61); H, 5.31 (5.24); Ir, 15.11 (15.02); S, 2.52 (2.41). Λ_M: 52 Ω^{-1} cm^2 mol^{-1}. IR: ν(Ir–H) 2090 (s) cm^{-1}. Complex **5** is stable in the solid state and in deaerated common organic solvents (THF, MeCN, acetone) at room temperature.

Reaction of 3a with Hydrogen. A solution of **3a** (0.20 g, 0.16 mmol) in THF (20 mL) was pressurized with hydrogen to 5 atm at room temperature in a Parr reactor for 3 h. After being depressurized and vented under a nitrogen stream, the contents of the bomb were transferred into a Schlenk-type flask. The volatiles were removed in vacuo. The pale yellow residue was crystallized from THF and ethanol, giving [(triphos)Ir(H)$_2${*o*-S(C$_6$H$_4$)C$_2$H$_5$}] (**8**) as off-white crystals. They were collected by filtration and washed with ethanol and *n*-pentane; yield 90%. Anal. Calcd (found) for $C_{49}H_{50}IrP_3S$: C, 61.55 (61.43); H, 5.27 (5.23); Ir, 20.10 (20.00); S, 3.35 (3.26). IR: ν(Ir–H) 2048 (s) cm^{-1}. No reaction was observed at 1 atm hydrogen pressure. In a parallel reaction, triphenylboron was separated from the residue by either sublimation (70 °C, 0.5 Torr) or extraction into *n*-pentane and authenticated (^{1}H NMR) by comparison with an authentic specimen. Complex **8** is thermally stable in deaerated THF solution up to 150 °C. The complex is air-stable only in the solid state.

Reaction of 3b with Hydrogen. Substitution of **3b** for **3a** and workup as above gave [(triphos)IrH(μ-*o*-S(C$_6$H$_4$)C$_2$H$_5$)$_2$HIr(triphos)](PF$_6$)$_2$ (**9b**) as a yellow solid; yield 80%. Anal. Calcd (found) for $C_{98}H_{98}F_{12}Ir_2P_8S_2$: C, 53.50 (53.21); H, 4.49 (4.42); Ir, 17.47 (17.19); S, 2.91 (2.78). IR: ν(Ir–H) 2100 (s) cm^{-1}. Λ_M: 154 Ω^{-1} cm^2 mol^{-1}. Complex **9b** is thermally stable in deaerated common organic solvents (THF, DMSO, MeCN, acetone) at reflux temperature. The complex is air-stable in both the solid state and solution.

Reaction of 8 with HCl. A sample of **8** (0.04 g, 0.04 mmol) was dissolved in 0.7 mL of CD_2Cl_2 and placed in a 5-mm NMR tube under nitrogen. The solution was frozen with liquid nitrogen, and a 2-fold excess of gaseous HCl was syringed into the tube, which was then allowed to reach room temperature. ^{31}P{^{1}H} and ^{1}H NMR spectra of this sample indicated the complete conversion of **8** to [(triphos)IrH(Cl)$_2$] (**10**)[17] and formation of H_2 (^{1}H NMR, singlet at 4.62 ppm) and free 2-ethylbenzenethiol[12] (^{1}H NMR: δ 3.41, s, *H*S; δ 2.71 q, C*H*$_2$CH$_3$; δ 1.26, t, *J*(HH) = 7.5 Hz, CH$_2$C*H*$_3$. GC/MS: EIMS, 70 eV [*m*/*e* (%)] 138 (84) M$^+$, 123 (100) M–CH$_3^+$, 105 (62) M–SH$^+$, 77 (45) C$_6$H$_5^+$).

Reaction of 8 with HBF$_4$. A stoichiometric amount of neat HBF$_4$·OEt$_2$ (*ca.* 45 μL) was syringed into a yellow solution of **8** (0.20 g, 0.21 mmol) in THF (30 mL) at room temperature. After 30 min, ethanol (10 mL) and *n*-heptane (20 mL) were added to the reaction mixture. On partial evaporation of the solvents under a brisk flow of nitrogen, yellow crystals of [(triphos)IrH(μ-*o*-S(C$_6$H$_4$)C$_2$H$_5$)$_2$HIr(triphos)](BF$_4$)$_2$ (**9c**) precipitated in 80% yield. Anal. Calcd (found) for $C_{98}H_{98}B_2F_8Ir_2P_6S_2$: C, 56.49 (56.38); H, 4.74 (4.74); Ir, 18.45 (18.35); S, 3.08 (2.89). IR: ν(Ir–H) 2100 (s) cm^{-1}. Λ_M: 149 Ω^{-1} cm^2 mol^{-1}. As the reaction was monitored by NMR spectroscopy in THF-d_8, dihydrogen evolution was also detected (^{1}H NMR: singlet at 4.7 ppm).

Synthesis of [(Triphos)IrH(η^2-*C*,*S*-C$_8$H$_6$S)] (11). To a stirred solution of **3a** (0.30 g, 0.24 mmol) in THF (30 mL) at *ca.* 0 °C was added a 4-fold excess of LiHBEt$_3$ (0.84 mL, 0.84 mmol). There was an immediate color change from red orange to pale yellow. After ethanol (*ca.* 5 mL) was added to destroy the excess of LiHBEt$_3$, the reaction mixture was allowed to reach room temperature. Addition of *n*-heptane (50 mL) and concentration gave sandy crystals of **11**, which were collected by filtration and washed with *n*-pentane; yield 80%. The reaction was also followed by ^{31}P{^{1}H} NMR spectroscopy in THF-d_8. The reaction occurred already at –70 °C; only the signals due to **3a** and **11** were observed. Anal. Calcd (found) for $C_{49}H_{46}IrP_3S$: C, 61.81 (61.77); H, 4.87 (4.83); Ir, 20.19 (20.00); S, 3.37 (3.25). IR: ν(Ir–H) 2082 (s); ν(C=C) 1574 (m) cm^{-1}. Compound **11** is rather unstable in solution at room temperature as it slowly converts to its isomer [(triphos)Ir(η^3-S(C$_6$H$_4$)CH=CH$_2$)] (**12**) (see below) (in THF at 20 °C, *ca.* 20% conversion occurs in 24 h). Solid samples of **11** are stable when stored under nitrogen at low temperature, whereas, at room temperature isomerization to **12** occurs also in the solid state (*ca.* 30% conversion in 1 month). Compound **11** is stable at room temperature under 5 atm hydrogen pressure in THF solution for 3 h.

Thermal Isomerization of 11 to [(Triphos)Ir(η^3-S(C$_6$H$_4$)CH=CH$_2$)] (12). A THF (30 mL) solution of **11** (0.24 g, 0.25 mmol) was heated at reflux temperature for *ca.* 24 h. After concentration under reduced pressure to *ca.* 10 mL, addition of *n*-heptane (30 mL) led to the precipitation of yellow crystals of **12** in 85% yield. Anal. Calcd (found) for $C_{49}H_{46}IrP_3S$: C, 61.81 (61.69); H, 4.87 (4.86); Ir, 20.19 (20.07); S, 3.37 (3.22). As the reaction was monitored in THF-d_8 by ^{31}P{^{1}H} NMR spectroscopy at 66 °C, clean conversion of **11** to **12** was observed ($t_{1/2}$ = 7 h). Compound **12** is stable at room temperature under 5 atm hydrogen pressure in THF solution. The compound is air-stable in both the solid state and solution.

Synthesis of [(Triphos)Ir(η^4-S(C$_6$H$_4$)C(H)Me)] (Y = BPh$_4$, 13a; BF$_4$, 13c). Addition of a stoichiometric amount of HBF$_4$·OEt$_2$ (*ca.* 60 μL) to a yellow solution of **12** (0.27 g, 0.28 mmol) in THF (30 mL) at *ca.* 0 °C immediately gave a deep red solution. After 30 min, the reaction mixture was allowed to warm to room temperature. On portionwise addition of *n*-heptane (20 mL), red crystals of **13c** precipitated in 80% yield. Anal. Calcd (found) for $C_{49}H_{47}BF_4IrP_3S$: C, 56.59 (56.43); H, 4.56 (4.43); Ir, 18.48 (18.24); S, 3.08 (2.89). Λ_M: 86 Ω^{-1} cm^2 mol^{-1}. The reaction was also followed by ^{31}P{^{1}H} NMR spectroscopy in THF-d_8. The reaction occurred already at –70 °C; only the signals due to **12** and **13c** were observed. Metathetical reaction of **13c** with NaBPh$_4$ in CH$_2$Cl$_2$/ethanol gave the tetraphenylborate salt **13a** in almost quantitative yield. Anal. Calcd (found) for $C_{73}H_{67}BIrP_3S$: C, 68.91 (68.00); H, 5.31 (5.14); Ir, 15.11 (14.89); S, 2.52 (2.43). Λ_M: 52 Ω^{-1} cm^2 mol^{-1}. The compounds are thermally stable in deaerated solvents such as THF, MeCN, and acetone at room temperature. At higher temperature, slow decomposition occurs. Also, the complexes are air-unstable in both the solid state and solution.

Reaction of 13a with Hydrogen. A. CH$_2$Cl$_2$. A red solution of **13a** (0.20 g, 0.16 mmol) in CH_2Cl_2 (20 mL) was stirred under hydrogen pressure (1–5 atm) at room temperature. After 3 h, the resulting yellow solution was concentrated to dryness under vacuum. The yellow residue was characterized by IR and NMR spectroscopy as [(triphos)IrH(μ-*o*-S(C$_6$H$_4$)C$_2$H$_5$)$_2$HIr(triphos)](BPh$_4$)$_2$ (**9a**). Anal. Calcd (found) for $C_{146}H_{138}B_2Ir_2P_6S_2$: C, 68.80 (68.58); H, 5.46 (5.51); Ir, 15.08 (14.98); S, 2.52 (2.47). IR: ν(Ir–H) 2100 (s) cm^{-1}. Λ_M: 99 Ω^{-1} cm^2 mol^{-1}.

B. THF. A red solution of **13a** (0.20 g, 0.16 mmol) in THF (20 mL) was stirred under hydrogen pressure (1–5 atm) at room temperature. After 3 h, a sample of the solution was withdrawn and analyzed by GC/MS, which showed almost quantitative formation of benzene. The rest of the solution was concentrated to dryness under vacuum, and the residue was found to contain [(triphos)Ir(H)$_2${*o*-S(C$_6$H$_4$)C$_2$H$_5$)}] (**8**) (IR and

(16) (a) Barbaro, P.; Bianchini, C.; Meli, A.; Peruzzini, M.; Vacca, A.; Vizza, F. *Organometallics* **1991**, *10*, 2227. (b) Siegl, W. O.; Lapporte, S. J.; Collman, J. P. *Inorg. Chem.* **1971**, *10*, 2158.

(17) Janser, P.; Venanzi, L. M.; Bachechi, F. *J. Organomet. Chem.* **1985**, *296*, 229.

NMR spectroscopy) and triphenylboron, which was separated from the residue by either sublimation (70 °C, 0.5 Torr) or extraction into *n*-pentane and authenticated (^{1}H NMR) by comparison with an authentic specimen.

Reaction of 13c with Hydrogen. A red solution of **13c** (0.20 g, 0.19 mmol) in THF (20 mL) was stirred under hydrogen pressure (1–5 atm) at room temperature. After 3 h, the resulting yellow solution was concentrated to dryness under vacuum. The yellow residue was characterized by IR and NMR spectroscopy as **9c**.

Synthesis of [(Triphos)IrH(η^2-S(C_6H_4)C(H)Me)] (14). To a stirred THF (30 mL) solution of $LiHBEt_3$ (0.68 mL, 0.68 mmol) at –70 °C was added a solid sample of **13c** (0.35 g, 0.34 mmol). The red solid immediately dissolved to give a pale yellow solution. After 15 min, the reaction mixture was allowed to reach room temperature, and then ethanol (10 mL) and *n*-heptane (30 mL) were added. On partial evaporation of the solvents under reduced pressure, compound **14** precipitated as sandy crystals, which were filtered off and washed with a cold 1:1 mixture of ethanol and *n*-pentane; yield 60%. Anal. Calcd (found) for $C_{49}H_{48}IrP_3S$: C, 61.68 (61.33); H, 5.07 (5.04); IR, 20.15 (20.03); S, 3.36 (3.14). IR: ν(Ir–H) 2132 (s) cm^{-1}. When the reaction in THF-d_8 was followed by ^{31}P{^{1}H} NMR spectroscopy at –70 °C, no intermediate species was detected along the conversion of **13c** to **14**.

Reaction of 14 with Hydrogen. A solution of **14** (0.20 g, 0.21 mmol) in THF (20 mL) was pressurized with hydrogen to 5 atm at room temperature in a Parr reactor. After 3 h, the contents of the bomb were transferred into a Schlenk-type flask and concentrated to dryness under vacuum. The residue was characterized by IR and NMR spectroscopy as **8**. No reaction was observed under 1 atm hydrogen pressure.

Reaction of 14 with HBF_4. A stoichiometric amount of neat HBF_4·OEt_2 (*ca.* 45 μL) was syringed into a yellow solution of **14** (0.20 g, 0.21 mmol) in THF (30 mL) at room temperature. After 30 min, ethanol (10 mL) and *n*-heptane (20 mL) were added to the reaction mixture. On slow evaporation of the solvents, yellow crystals of **9c** precipitated in 80% yield.

X-ray Data Collection and Structure Determination of 3a·1.5THF·0.5EtOH. A red-orange parallelepiped crystal was mounted on a glass fiber on a Philips PW1100 automatic diffractometer. Unit cell dimensions were determined from least-squares refinement of the angular settings of 25 carefully centered reflections. As a general procedure, three standard reflections were collected every 2 h (no decay of intensities was observed in any case). Intensity data were corrected for Lorentz-polarization effects. Atomic scattering factors were those tabulated by Cromer and Waber[18] with anomalous dispersion correction taken from ref 19. Absorption correction was applied by using the DIFABS program.[20] All the calculations were carried out on a Digital DEC 5000/200 computer by using the SHELX76 program.[21] The structure was solved by heavy-atom techniques. Refinement was done by full-matrix least-squares calculations initially with isotropic thermal parameters. Anisotropic thermal parameters were used for iridium and phosphorus atoms only. The phenyl rings were treated as rigid bodies of D_{6h} symmetry (C–C = 1.39 Å) and calculated hydrogen atom positions (C–H = 1.08 Å). THF and ethanol solvent molecules were located at an advanced stage of refinement. All the atoms were treated as carbon atoms. Ethanol and one of the THF solvent molecules were assigned a population factor of 0.5. Crystallographic and other relevant data collection are reported in Table 3.

Results

The preparations and the principal reactions of the complexes described in this paper are illustrated in Schemes 1–6. Selected NMR spectral data are collected in Table 1 (^{31}P{^{1}H} NMR) and Table 2 (^{1}H, ^{13}C{^{1}H} NMR). ^{13}C-DEPT, ^{13}C–^{1}H 2D-HETCOR, and ^{1}H–^{1}H 2D-COSY spectra allowed the total and unequivocal assignment of all ^{1}H and ^{13}C resonances for all compounds as labeled on Table 2.

Coordination and Opening of Benzo[*b*]thiophene at the [(triphos)Ir]$^+$ Fragment. Stirring THF solutions of the η^4-benzene complexes [(triphos)Ir(η^4-C_6H_6)]Y (Y = BPh_4, **1a**; PF_6, **1b**] with an excess of BT at 25 °C slowly results in quantitative evolution of benzene and formation of the η^3-*C*,*C*,*S*-BT complexes [(triphos)-Ir(η^3-*C*,*C*,*S*-C_8H_6S)]Y [Y = BPh_4, **2a**; PF_6, **2b**]. The intact BT ligand in **2a,b** (see below) is cleaved as soon as THF solutions of these compounds are heated above 40 °C. As a result, iridium inserts into a C–S bond from the coordinated BT to give the iridabenzothiabenzene complexes [(triphos)Ir(η^2-*C*,*S*-C_8H_6S)]Y [Y = BPh_4, **3a**; PF_6, **3b**]. Under our observational conditions (^{31}P and ^{1}H NMR spectroscopy), no intermediate species was detected along the transformations of either **1a,b** into **2a,b** or **2a,b** into **3a,b**.

Scheme 1

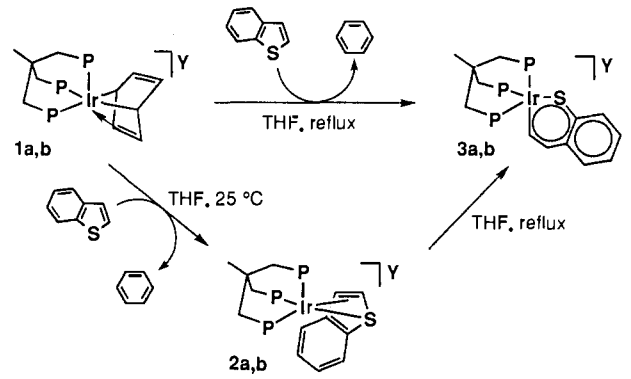


Table 1. ^{31}P{^{1}H} NMR Spectral Data for the New Complexes[a]

complex	pattern	chem shift, ppm[b] $\delta(P_A)$	$\delta(P_M)$	$\delta(P_Q)$	coupling const, Hz $J(P_AP_M)$	$J(P_AP_Q)$	$J(P_MP_Q)$
2$^+$	AM_2	–1(br)	–9(br)				
	AMQ[c]	–0.7	–8.0	–9.2	11.0	6.2	17.0
3$^+$	A_3	–0.5(br)					
	AM_2[d]	–11.2	4.9		14.6		
5$^+$	AM_2	0.3	–16.4		16.6		
8	AM_2	–2.3	–25.3		14.4		
9^{2+}	AM_2	3.3(br)	8.8(br)				
	AM_2[e]	3.6	9.0		9.2		
11	AMQ	–5.3	–32.7	–51.1	16.6	13.0	14.6
12	AMQ	–11.2	–28.4	–35.4	21.8	17.5	34.2
13$^+$	A_3	–6.5(br)					
	AM_2[f]	1(br)	–11(br)				
	AMQ[e]	1(br)	–8(br)	–13(br)			
	AMQ[d]	–3.4	–12.0	–23.4	26.8	18.6	<1
14	AMQ	–3.1	–27.2	–50.4	16.3	8.5	17.4

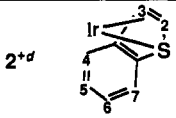
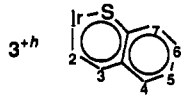
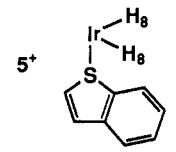
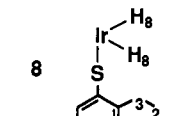
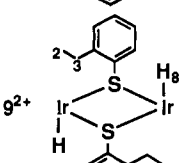
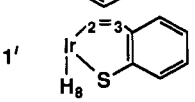
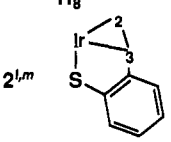
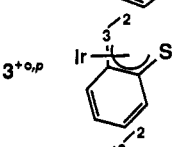
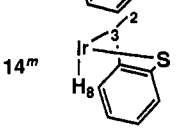
[a] All spectra were recorded at 20 °C in CD_2Cl_2 solutions unless otherwise stated. [b] The chemical shifts (δ's) are relative to 85% H_3PO_4; downfield values are assumed as positive. [c] Al –30 °C. [d] At –70 °C. [e] At –10 °C. [f] At 0 °C.

An X-ray diffraction analysis has been carried out on crystals of **3a**·1.5THF·0.5EtOH obtained by slow diffusion techniques from THF/EtOH. Figure 1 shows an ORTEP view of the complex cation. Selected bond distances and angles are collected in Table 4.

The P_3Ir grouping of the (triphos)Ir fragment has an approximate C_{3v} symmetry with three P–Ir–P angles in the range 86.9(1)–89.8(1)°.[17] The η^2-*C*,*S*-C_8H_6S ligand is oriented in such a way that one Ir–P bond lies in the plane of the BT-derived ligand. Accordingly, the coordination geometry approximates a trigonal-bipyramid with the sulfur and carbon atoms occupying equatorial and apical positions, respectively (P_1–Ir–C_6 = 177.7-(3), S_1–Ir–C_6 91.6(3)°). However, some distortion from the idealized structure is clearly evident (P_3–Ir–S_1 = 136.3(1), P_2–Ir–P_3 = 86.9(1)°). As observed for other iridium complexes with triphos,[22] the two equatorial Ir–P bond lengths are equivalent (2.265(3) and 2.260(3) Å) and shorter than the axial one (2.395-(3) Å).

(18) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.
(19) International Tables of Crystallography; Kynoch: Birmingham, England, 1974; Vol. 4.
(20) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.
(21) Sheldrick, G. M. SHELX76 Program for Crystal Structure Determinations; University of Cambridge: Cambridge, England, 1976.
(22) Bianchini, C.; Caulton, K. G.; Folting, K.; Meli, A.; Peruzzini, M.; Polo, A.; Vizza, F. *J. Am. Chem. Soc.* **1992**, *114*, 7290.

Table 2. Selected NMR Spectral Data for the New Complexes[a]

complex	^{1}H NMR assignt	^{1}H NMR δ (multiplicity, J)[b,c]	^{13}C{^{1}H} NMR assignt	^{13}C{^{1}H} NMR δ (multiplicity, J)[b]
 **2**$^{+d}$	H_2	8.02 (qd, $^3J(H_2H_3)$ = 2.9, $^3J(H_2P)$ = 3.7)	C_2	73.0 (dd, $^2J(C_2P)$ = 14.6, 7.2)
	H_4	7.2[e]	C_3	42.3 (dd, $^2J(C_3P)$ = 18.6, 8.6)
	H_6	7.0[e]	C_5	124[f]
	H_7	6.9[e]	C_4	*g*
	H_5	6.63 (td, $^3J(H_5H_4)$ = $^3J(H_5H_6)$ = 7.4, $^4J(H_5H_7)$ = 1.2)	C_6	*g*
	H_3	2.85 (d)	C_7	*g*
 **3**$^{+h}$	H_4	8.46 (brd, $^3J(H_4H_5)$ = 7.6, $^4J(H_4H_6)$ = 1.4)	C_2	162.1 (q, $^2J(C_2P)$ = 21.1)
	H_2	8.33 (dq, $^3J(H_2H_3)$ = 11.2, $^3J(H_2P)$ = 7.0)	C_7	134.3 (s)
	H_3	8.26 (m, $^4J(H_3P)$ = 5.8)	C_4	133[f]
	H_7	7.83 (dd, $^3J(H_6H_6)$ = 7.9, $^4J(H_7H_5)$ = 1.6)	C_3	129.9 (s)
	H_6	7.74 (brt, $^3J(H_6H_5)$ = 7.3)	C_6	128.5 (s)
	H_5	7.63 (td)	C_5	127.11 (s)
 **5**$^+$	H_8	−9.62 (dm)[i]	C_{BT}	136.2 (s), 127.8 (s), 124.9 (s), 124.6 (s), 122.3 (s), 121.4 (s), *g*, *g*
 **8**	H_3	2.84 (q, $^3J(H_3H_2)$ = 7.5)		
	H_2	1.16 (t)		
	H_8	−9.17 (dm)[j]		
 **9**$^{2+}$	H_3	2.98 (q, $^3J(H_3H_2)$ = 7.5)		
	H_2	1.30 (t)		
	H_8	−1.43 (dm)[k]		
 **11**′	H_2	6.42 (m, $^3J(H_2H_3)$ = 11.1, $^3J(H_2P)$ = 15.1, 7.0, 4.1)	C_2	134[f]
	H_3	6.8[e]	C_3	*g*
	H_8	−8.63 (dt, $^2J(H_8P)$ = 165.0, 7.8)		
 **12**^{l,m}	H_3	3.04 (m, $^3J(H_3H_2)$ = $^3J(H_3H_{2'})$ = 7.7, $^3J(H_3P)$ = 5.3, 5.3, 4.0)	C_3	50.3 (ddd, $^2J(C_3P)$ = 34.6, 7.6, 1.5)
	$H_{2'}$	2.1[n]	C_2	25.2 (ddd, $^2J(C_2P)$ = 43.0, 6.8, 2.0)
	H_2	1.81 (m, $^2J(H_2H_{2'})$ = 1.5)		
 **13**$^{+o,p}$	H_3	3.52 (q, $^3J(H_3H_2)$ = 6.6)	C_3	58.7 (q, $^2J(C_3P)$ = 17.5)
	H_2	0.31 (dq, $^4J(H_2P)$ = 3.7)	C_2	20.9 (s)
 **14**^{m}	H_3	2.5[n]	C_3	33.0 (dt, $^2J(C_2P)$ = 69.9, 4.4)
	H_2	1.34 (t, $^3J(H_2H_3)$ = 6.8, $^3J(H_2P)$ = 6.3)	C_2	13.6 (s)
	H_8	−10.00 (dt, $^2J(H_8P)$ = 176.2, 12.2)		

[a] All spectra were recorded at room temperature in CD_2Cl_2 solutions at 200.13 (^{1}H NMR) and 50.32 MHz (^{13}C{^{1}H} NMR) unless otherwise stated. [b] Chemical shifts are given in ppm and are relative to either residual ^{1}H resonance in the deuterated solvent (^{1}H NMR) or the deuterated solvent resonance (^{13}C{^{1}H} NMR). Key: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, br, broad. Coupling constants (*J*) are in hertz. [c] The *J*(HH) values were determined on the basis of ^{1}H{^{31}P} NMR experiments. [d] ^{1}H NMR, −40 °C: δ 8.00 (dd, $^3J(H_2P)$ = 9.9 Hz, $^3J(H_2H_3)$ = 2.9 Hz, H_2); δ 2.81 (m, $^3J(H_3P)$ = 5.0 Hz, H_3). [e] Masked by the aromatic protons of the triphos ligand and of the BPh_4^- anion. The chemical shift was determined from ^{1}H, ^{1}H 2D-COSY experiment. [f] Masked by the phenyl carbons of the triphos ligand and of the BPh_4^- anion. The chemical shift was determined from ^{13}C, ^{1}H heteronuclear 2D-NMR correlation study. [g] The chemical shift (aromatic carbon region) could not be determined. [h] The ^{1}H NMR spectrum was recorded at 600.14 MHz. [i] Second-order doublet of multiplets, AA′XX′Y spin system, $|^2J(HP_M) + {}^2J(HP_{M'})|$ = 114.1 Hz, $^2J(HP_A)$ = 10.6 Hz. [j] Second-order doublet of multiplets, AA′XX′Y spin system, $|^2J(HP_M) + {}^2J(HP_{M'})|$ = 132.6 Hz, $^2J(HP_A)$ = 12.1 Hz. [k] At −10 °C, δ −1.34 (dt, $^2J(H_8P)$ = 132.2, 10.2 Hz). [l] The ^{1}H NMR spectrum was recorded in THF-d_8. [m] The ^{13}C{^{1}H} NMR spectrum was recorded in THF-d_8. [n] Masked by the aliphatic protons of triphos. The chemical shift was determined from ^{1}H,^{1}H 2D-COSY experiment. [o] At −70 °C, the ^{1}H NMR signals of the H_3 and H_2 hydrogens appear as broad multiplets at 3.3 and −0.5 ppm, respectively. [p] The ^{13}C{^{1}H} NMR spectrum was recorded in acetone-d_6; coordinated quaternary carbons: δ 120.3 (d, ^2J(CP) = 9.1 Hz), 110.6 (d, ^2J(CP) = 7.6 Hz).

Of particular interest is the bonding within the metallacycle Ir–C_6–C_7–C_8–C_{13}–S_1. The metallacycle is planar: the mean deviation from the plane defined by atoms Ir, C_6, C_7, C_8, C_{13}, and S_1 is only 0.003 Å (the entire ring system comprising Ir, C_6, C_7, C_8, C_9, C_{10}, C_{11}, C_{12}, C_{13}, and S_1 is planar with a mean deviation of only 0.017 Å from planarity). The bond distances within the six-membered metallaring are suggestive of a delocalized π-bonding system (C_6–C_7 = 1.36(2), C_7–C_8 = 1.44(1), C_8–C_{13} = 1.41(1), Ir–C_6 = 2.07(1), Ir–S_1 = 2.243(3), C_{13}–S_1 = 1.71(1) Å), which is confirmed by the NMR data (vide infra).

Direct comparisons with other metal complexes are precluded by the lack of mononuclear metallabenzothiabenzene complexes in the literature. However, it may be useful to compare the structure of **3a** with those of Cp*Ir(η^2-*C*,*S*-2,5-Me_2T)[23] described by Angelici and of *mer*-$(Me_3P)_3Ir(SC_8H_6)Cl$ described by Merola.[11] In the former complex, a Cp*Ir unit is in place of the isolobal (triphos)Ir fragment, while 2,5-dimethylthiophene is substituted for BT. Accordingly, the electronic situation of

(23) Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 199.

Table 3. Summary of Crystal Data for **3a**·1.5THF·0.5EtOH

formula	$C_{80}H_{80}BIrO_2P_3S$
formula weight	1401.54
crystal dimensions, mm	0.17 × 0.35 × 0.42
crystal system	triclinic
space group	$P\bar{1}$ (no. 2)
a, Å	17.391(3)
b, Å	16.957(4)
c, Å	12.795(3)
α, deg	77.51(2)
β, deg	80.98(2)
γ, deg	75.50(2)
V, Å^3	3545.51
Z	2
d_{calcd}, g cm^{-3}	1.31
μ(Cu Kα), cm^{-1}	48.27
radiation	graphite-monochromated Cu Kα, λ = 1.5418 Å
scan type	ω–2θ
2θ range, deg	5–110
scan width, deg	0.9 + 0.15(tan θ)
scan speed, deg s^{-1}	0.06
total no. of data	8938
no. of unique data, $I > 3\sigma(I)$	7636
no. of parameters	276
R	0.072
R_w	0.079
abs. correction, min.–max.	0.77–1.22

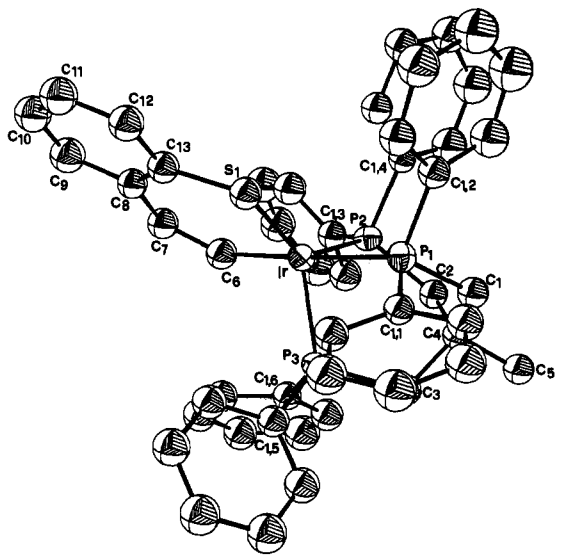


Figure 1. ORTEP drawing of the complex cation in **3a**·1.5THF·0.5EtOH. All of the hydrogen atoms are omitted for clarity.

Angelici's compound is substantially similar to the one of our BT-derived complex. As a matter of fact, the bond distances and angles within these two metallacycles are more similar than in Merola's complex, where an additional 2e-donor bonded to iridium causes a more localized structure.

Since the counteranion does not influence at all the spectroscopic properties of **2a**,**b** and **3a**,**b**, the relevant NMR data reported in Tables 1 and 2 refer to the complex cations [(triphos)Ir(η^3-*C*,*C*,*S*-C_8H_6S)]$^+$ and [(triphos)Ir(η^2-*C*,*S*-C_8H_6S)]$^+$, hereafter quoted as **2**$^+$ and **3**$^+$, respectively.

In solution, both complexes are stereochemically nonrigid on the NMR time scale. However, the fluxionality essentially involves only the phosphorus donors and not the C_8H_6S ligands, which in fact show no variation of the chemical shifts of their hydrogen and carbon nuclei, whereas the multiplicity originated by coupling to the phosphorus atoms evidently changes with the temperature.

In the slow exchange regime, attained at *ca.* –30 °C in CD_2Cl_2, the $^{31}P\{^1H\}$ NMR spectrum of **2**$^+$ consists of a well-resolved AMQ pattern, which shows the three phosphorus nuclei to be magnetically inequivalent (δP_A –0.7, δP_M –8.0, δP_Q –9.2) as is observed when the phosphorus donors of triphos have different trans ligands.[16a,24] As the temperature is increased, broadening of all resonances takes place. At 20 °C, the spectrum consists of two humps centered at –1 and –9 ppm in a relative intensity ratio of 1 to 2. Both resonances coalesce into the baseline at *ca.* 30 °C. At higher temperature (THF-d_8 solution), decoalescence occurs to give a single resonance at –6.2 ppm (A_3 spin system), which at 60 °C exhibits a $w_{1/2}$ value of 42 Hz.

Table 4. Selected Bond Distances (Å) and Angles (deg) for **3a**·1.5THF·0.5EtOH

Ir–P_1	2.395(3)	S_1–C_{13}	1.71(1)
Ir–P_2	2.265(3)	C_1–C_4	1.51(1)
Ir–P_3	2.260(3)	C_2–C_4	1.57(2)
Ir–S_1	2.243(3)	C_3–C_4	1.56(2)
Ir–C_6	2.07(1)	C_4–C_5	1.52(1)
P_1–C_1	1.83(1)	C_6–C_7	1.36(2)
P_1–$C_{1,1}$	1.829(8)	C_7–C_8	1.44(1)
P_1–$C_{1,2}$	1.824(9)	C_8–C_9	1.43(2)
P_2–C_2	1.82(1)	C_8–C_{13}	1.41(1)
P_2–$C_{1,3}$	1.817(9)	C_9–C_{10}	1.36(2)
P_2–$C_{1,4}$	1.819(9)	C_{10}–C_{11}	1.34(2)
P_3–C_3	1.84(1)	C_{11}–C_{12}	1.40(2)
P_3–$C_{1,5}$	1.823(8)	C_{12}–C_{13}	1.40(2)
P_3–$C_{1,6}$	1.825(7)		
P_1–Ir–P_2	88.5(1)	P_3–Ir–C_6	92.3(3)
P_1–Ir–P_3	89.8(1)	S_1–Ir–C_6	91.6(3)
P_1–Ir–S_1	87.6(1)	Ir–S_1–C_{13}	117.7(4)
P_1–Ir–C_6	177.7(3)	S_1–C_{13}–C_8	125.5(9)
P_2–Ir–P_3	86.9(1)	C_{13}–C_8–C_7	124(1)
P_2–Ir–S_1	136.5(1)	C_8–C_7–C_6	132(1)
P_2–Ir–C_6	90.6(3)	C_7–C_6–Ir	128.8(9)
P_3–Ir–S_1	136.3(1)		

The fluxional behavior exhibited by the iridabenzothiabenzene complex **3**$^+$ is significantly different from that of the precursor **2**$^+$. On the ^{31}P NMR time scale, the slow exchange regime is attained at a much lower temperature (–70 °C in CD_2Cl_2) and the spectrum consists of a resolved AM_2 spin system with J(PP) = 14.6 Hz. As the temperature is increased, both resonances broaden and then at –30 °C coalesce. At room temperature, a single resonance centered at –0.5 ppm emerges from the baseline, which sharpens for a further increase of the temperature ($w_{1/2}$ = 9 Hz at 60 °C in THF-d_8).

The overall dynamic behavior of **3**$^+$ nicely resembles that of the related iridathiabenzene complex [(triphos)Ir(η^2-*C*,*S*-C_4H_4S)]-BPh_4 studied in detail by computer simulation with the use of the DNMR3 program.[25] The magnetic equivalence of the three phosphorus atoms of **3**$^+$ in the fast exchange regime is thus attributed to a fast non-bond-breaking interconversion between trigonal-bipyramidal and square-pyramidal structures.[26] The spectrum in the slow exchange regime is in agreement with a trigonal-bipyramidal geometry which, consistently, is the preferred one in the solid state, as shown by the X-ray diffraction analysis.

On the basis of ^{31}P NMR spectroscopy alone, it is not possible to state that **2**$^+$ contains an intact BT molecule. Conversely, the ^1H and ^{13}C NMR data, particularly those referring to the C_2–H_2 and C_3–H_3 groupings, can be translated into strong evidence for an η^3-*C*,*C*,*S* bonding mode of an intact BT ligand.

In the iridabenzothiabenzene complex **3**$^+$, the positions of the carbon and hydrogen (Figure 2) resonances within the metallacycle are in the proper range for delocalized six-membered thiametallarings,[23,27] a related example of which is contained in the thiophene-derived complex [(triphos)Ir(η^2-*C*,*S*-C_4H_4S)]-BPh_4.[25] In contrast, the resonance of H_3 in **2**$^+$ moves largely

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(25) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P.; Herrera, V.; Sánchez-Delgado, R. A. *J. Am. Chem. Soc.* **1993**, *115*, 2731.
(26) (a) Bianchini, C.; Masi, D.; Mealli, C.; Meli, A.; Martini, G.; Laschi, F.; Zanello, P. *Inorg. Chem.* **1987**, *26*, 3683. (b) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.
(27) Jones, W. D.; Chin, R. M. *J. Am. Chem. Soc.* **1992**, *114*, 9851.

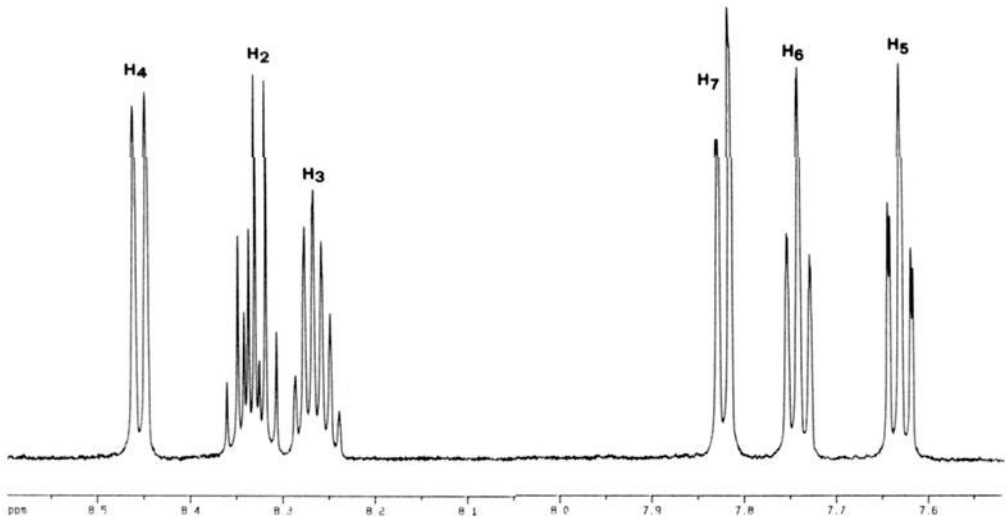
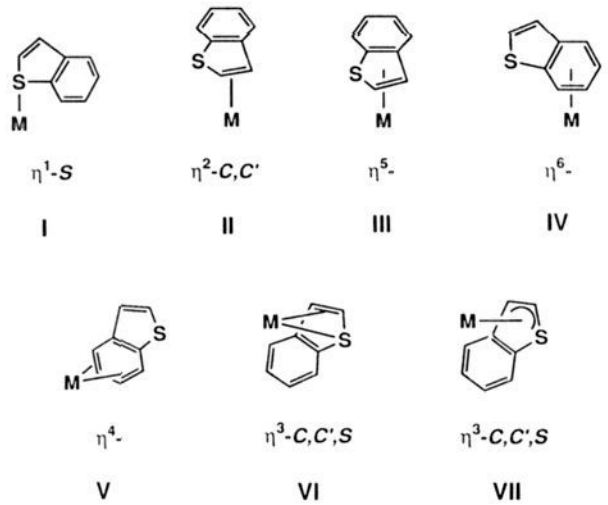


Figure 2. ^1H NMR spectrum of BT protons in 3^+ in CD_2Cl_2 at 20 °C (600.14 MHz).

Chart 1



upfield (δ 2.85, $J(H_3H_2)$ = 2.9 Hz). In a similar way, the resonances of the C_2 and C_3 nuclei in 2^+ (δ 73.0 and 42.3, respectively) are largely shifted to high field as compared to the analogous resonances in 3^+ (δ 162.1 and 129.9, respectively). These spectral features, together with the observation that appreciable coupling to the phosphorus nuclei in 2^+ is found only for the H_2 and H_3 hydrogen atoms and for the C_2 and C_3 carbons, rule out alternative structures such as a different type of metalacycle or an η^1-S bonding mode (**I**) (Chart 1).[7] An η^2-coordination through the C_2–C_3 double bond[7b,c] without involvement of the sulfur atom (**II**) is excluded in view of the upfield shift observed uniquely for the H_3 hydrogen atom as well as the electronic deficiency of the resulting complex. Electronic reasons (20-e species) also rule out either an η^5-coordination mode through the thiophenic portion of BT (**III**) or an η^6-coordination through the arene moiety (**IV**).[5] It remains to consider an η^4-arene bonding mode,[6b] as shown in sketch **V**. Also, this possibility can readily be excluded through a comparison of the ^1H and $^{13}C\{^1H\}$ NMR spectra of 2^+ with those of $Cp^*Ir(\eta^4$-3-MeBT).[6b] The iridium center in 2^+ is thus coordinated to the S, C_2, and C_3 atoms of BT. The η^3-bonding mode via the S and olefin may be rigid, as shown in sketch **VI**, or delocalized, as shown in sketch **VII**. Actually, just the chemical shifts of the H_2 (δ 8.02), C_2 (δ 73.0), H_3 (δ 2.85), and C_3 (δ 42.3) nuclei suggest a pseudoallylic structure for

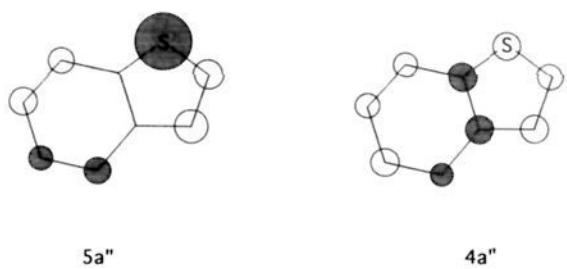


Figure 3. Frontier orbitals of the BT molecule.

2^+ (**VII**) rather than a rigid η^3-coordination (**VI**).[28] On the other hand, the potential of BT to act as an allyl-type η^3-*C,C',S* ligand is suggested by MO calculations. On the other hand, the potential of BT to act as an allyl-type η^3-*C,C',S* ligand is suggested by MO calculations. Some of us recently reported SCF-CNDO/2 calculations on the BT molecule, which show that the highest electron densities are located on the S and C_2 atoms.[10c] Another set of calculations (extended Hückel) indicate that the highest electron densities are on the S and the C_3 atoms of BT.[29] It is perhaps more instructive to consider the frontier orbitals of BT, particularly the occupied MO's represented in Figure 3, since this molecule acts as an electron donor from its π-system to the metal. The HOMO (5a″) is highly localized on the S atom, with a small bonding C_2–C_3 contribution; this orbital corresponds essentially to what is commonly viewed as the S π-lone pair. Slightly lower in energy is found the orbital 4a″, which contains S–C_2 and C_2–C_3 bonding interactions;[10c] the symmetry of this 4a″ orbital (see Figure 3) is particularly adequate for the η^3-*C,C',S* bonding mode we are proposing.

Additional experimental evidence for the presence of an intact BT molecule in 2^+ and of a cleaved BT ligand in 3^+ is provided by a comparison of the reactivity of both compounds toward CO and H_2 (the reactions with H_2 are discussed in the following section).

Complex **2a** reacts with CO (1 atm) at room temperature to give the dicarbonyl $[(triphos)Ir(CO)_2]BPh_4$[16] (**4**) and free BT, whereas **3a** requires the use of 5 atm of CO at 70 °C to eliminate BT and convert to **4**. The use of drastic reaction conditions to induce the reductive elimination of BT has previously been observed by Rauchfuss for the conversion of the benzothiaferrole $Fe_2(C_8H_6S)(CO)_6$ to $Fe(CO)_5$.[12a]

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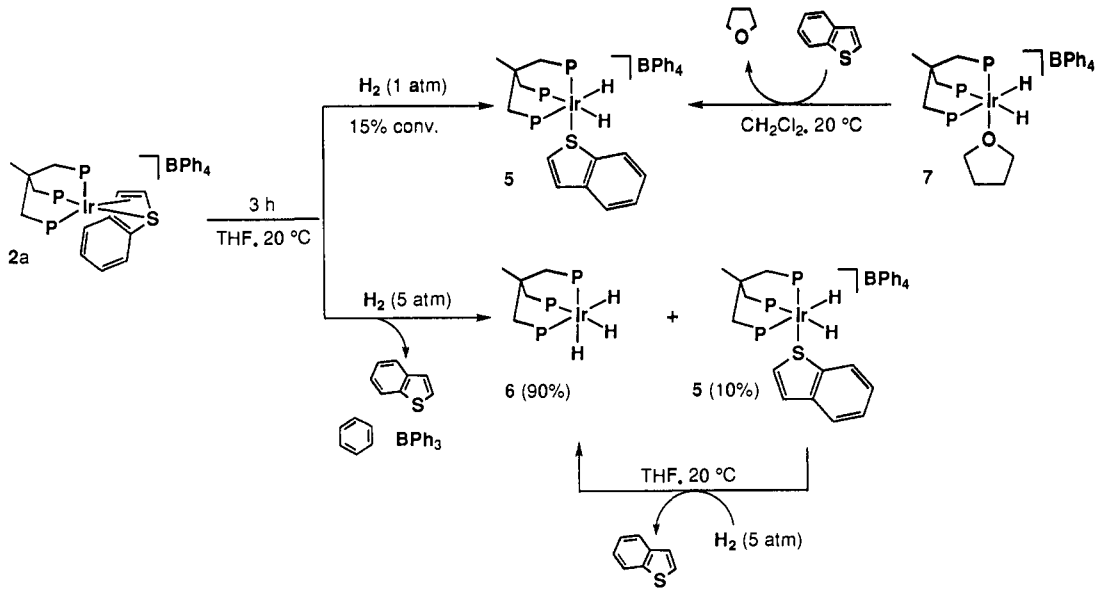
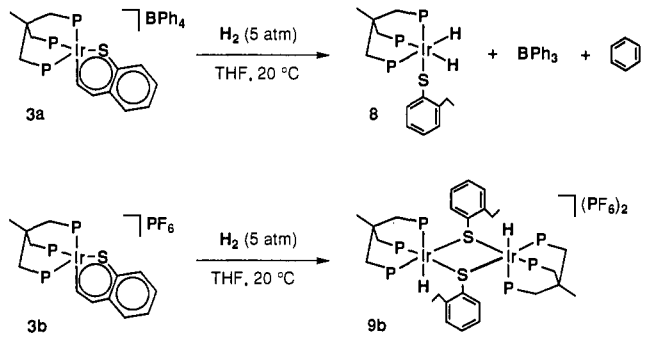
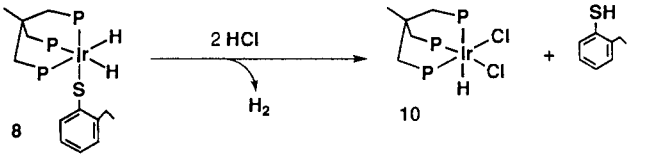
Scheme 2



Scheme 3



Scheme 4



Hydrogenation of Intact and Cleaved BT Ligands. Compound **2a** in THF reacts with H_2 (1 atm) at 20 °C, slowly converting to the η^1-*S*-BT dihydride [(triphos)Ir(H)$_2$(η^1-*S*-BT)]BPh_4 (**5**), which can independently be prepared by treatment of the THF-adduct [(triphos)Ir(H)$_2$(THF)]BPh_4 (**7**) with BT (Scheme 2).

At higher H_2 pressure (5 atm), the reaction is much faster and practically yields the trihydride [(triphos)IrH_3][7] (**6**) and BT. No trace of dihydrobenzothiophene was observed. The trihydride **6** is formed from **5** and, as previously reported, is the product of a heterolytic splitting of H_2 taking place at the [(triphos)Ir-(H)$_2$]$^+$ fragment and assisted by the BPh_4^- counteranion.[30] The latter, in fact, reacts with H^+ generated in the course of the heterolytic splitting, to give triphenylboron and benzene.

The reaction of the iridabenzothiabenzene isomer **3a** with H_2 is much more interesting (Scheme 3). Hydrogenation of the cleaved BT ligand rapidly occurs at room temperature and 5 atm of H_2. As a result, the BT ligand incorporates three hydrogen atoms and converts to 2-ethylbenzenethiolate, which coordinates the metal center via the sulfur atom. In the resulting complex [(triphos)Ir(H)$_2${*o*-S(C_6H_4)C_2H_5}] (**8**), the octahedral coordination around the metal is completed by two terminal hydride ligands [ν(Ir–H) 2048 cm^{-1}] and by the three phosphorus atoms of triphos. Ultimately, free 2-ethylbenzenethiol can be obtained from **8** by treatment with 2 equiv of HCl (Scheme 4).

Like in **8**, the metal center in **5** is octahedrally coordinated by the three phosphorus atoms of triphos ($^{31}P\{^1H\}$ NMR AM_2 pattern), by two terminal hydride ligands [ν(Ir–H) 2090 cm^{-1}], and by a sulfur atom from BT. As commonly observed for stereochemically rigid dihydrido metal complexes of the formula [(triphos)Ir(H)$_2$L]$^{n+}$ (L = monodentate ligands; n = 0, 1), the two hydride ligands in **5** and **8** are chemically but not magnetically equivalent and thus give rise to second-order doublets of multiplets (AA′XX′Y spin system, A = H; X,Y = P).[16a,24a]

Along the hydrogenation reaction that converts **3a** to **8**, a proton is apparently generated as we observe decomposition of the BPh_4^- counteranion to BPh_3 and C_6H_6. In this reaction, therefore, the counteranion has a non-innocent behavior. The non-innocent role of the counteranion is clearly shown by the reaction of **3b** with H_2 under identical conditions. As is illustrated in Scheme 3, a dimeric complex, [(triphos)IrH{μ-*o*-S(C_6H_4)C_2H_5}$_2$HIr-(triphos)] (PF_6)$_2$ (**9b**), is now formed where two 2-ethylbenzenethiolate ligands bridge (triphos)IrH moieties. The dimer **9b** is slightly fluxional in ambient-temperature solutions on the NMR time scale, as shown by the $^{31}P\{^1H\}$ NMR spectrum which shows an AM_2 pattern with no discernible J(PP). Such coupling constants are observed in the slow exchange regime spectrum attained at −10 °C. At this temperature, the resonance of the terminal hydride ligand bonded to each metal center appears as a doublet of triplets. Stereochemical nonrigidity is frequently encountered in μ-SR binuclear complexes and is attributed to the flexibility of the thiolate bridges.[31] Compound **9b** is formed by dimerization of unsaturated [(triphos)Ir(H){S(C_6H_4)C_2H_5}]$^+$ fragments (vide infra). The preference for bridging thiolates over bridging hydrides is a well-known process which is generally governed by electronic factors, i.e. the formation of a three-center-four-electron system is preferred over a three-center-two-electron interaction.[32]

Having found that the hydrogenation reaction of **3a** to **8** involves a heterolytic mechanism, it seemed interesting to us to determine at which stage of the hydrogenation path the heterolytic cleavage occurs. The question is not of trivial importance, as the existence

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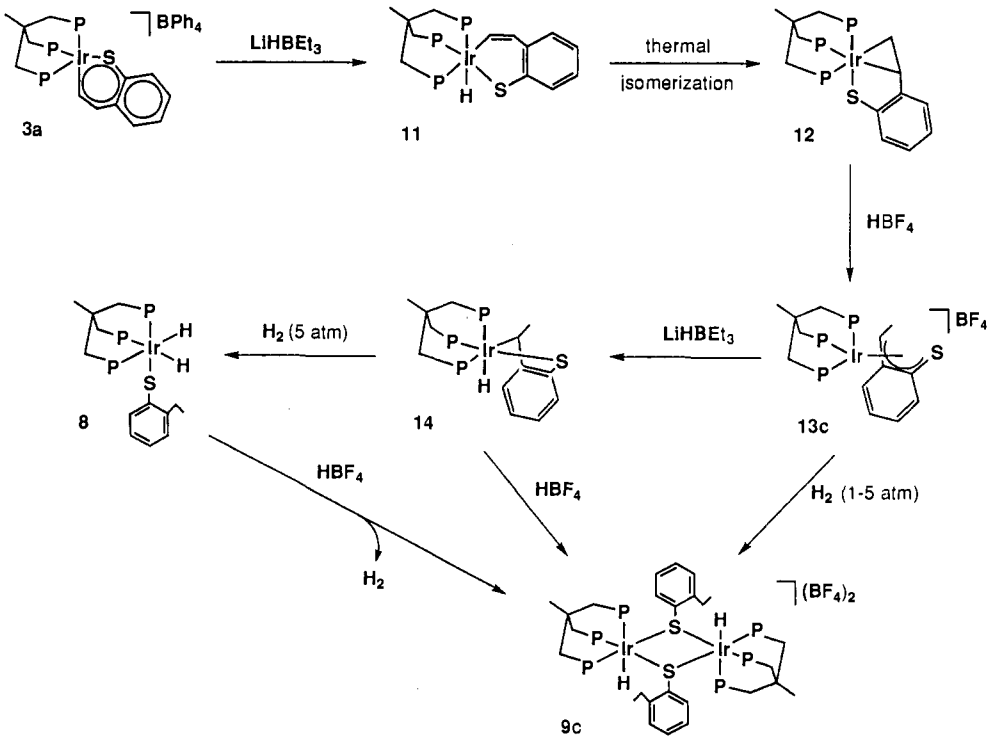
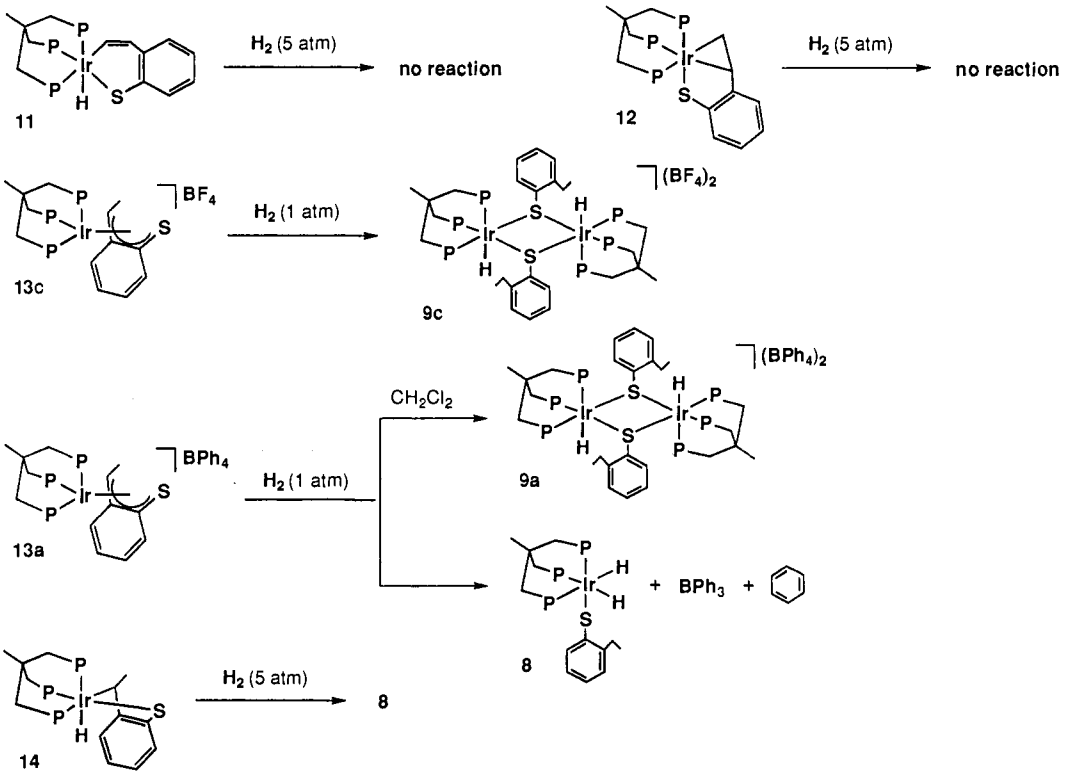
Scheme 5. All Reactions Were Performed in THF



Scheme 6. All Reactions Were Performed in THF at 20 °C, unless Otherwise Stated



of heterolytic reaction mechanisms in hydrotreating catalysis has recently been proposed.[4a,33]

In order to unravel this mechanistic point, the iridabenzothiabenzene complex **3a** in THF was treated with sequential additions of H^- and H^+ and the isolated product of each single addition reacted with H_2. The results of our study are summarized in Schemes 5 and 6.

Stepwise Hydrogenation of the Iridabenzothiabenzene Complex. Compound **3a** reacts with $LiHBEt_3$ to give quantitatively sandy crystals of [(triphos)IrH(η^2-*C,S*-C_8H_6S)] (**11**). As a consequence of hydride coordination, the resulting complex becomes stereochemically rigid on the NMR time scale (^{31}P AMQ pattern), and the pseudoaromaticity of the thiabenzene precursor is dismissed. Indeed, a localized electronic structure with a double bond bond between C_2 and C_3 is unambiguously shown by the ^{13}C high-field shift of C_2 from 162 ppm in **3a** to 134 ppm in **11** as well as the presence of a ν(C=C) band at 1574 cm^{-1} in the IR spectrum. All the spectroscopic data of **11** are in good

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correlation with those of related complexes such as *mer*-$(Me_3P)_3Ir(SC_8H_6)Cl$,[11] *mer*-$(Ir{-}CH{=}CH{-}CH{=}CH{-}S)(PEt_3)_3H$,[34] $Cp^*Ir(\eta^2\text{-}C,S\text{-}2,5\text{-}Me_2T)L$ (L = PMe_2Ph, $PMePh_2$, CO),[35] $Cp^*Rh(PMe_3)(SC_8H_6)$,[8] and [(triphos)IrH(η^2-*C,S*-C_4H_4S)].[25] Like the latter compound, **11** is thermally unstable in solution and converts to [(triphos)Ir(η^3-$S(C_6H_4)CH{=}CH_2$)] (**12**) as a result of selective delivery of hydride from metal to the C_2 carbon atom (δ 25.2), which now bears two gem hydrogens [$\delta H_{2'}$ 2.04, δH_2 1.81, $^2J(H_2H_{2'})$ = 1.5 Hz]. In complex **12**, which is stereochemically rigid (^{31}P AMQ pattern), the olefinic end of the BT-derived ligand is strongly bound to iridium [$^2J(C_3P)$ = 34.6, 7.6, 1.5 Hz; $^2J(C_2P)$ = 43.0, 6.8, 2.0 Hz]. The ^{1}H and ^{13}C NMR parameters are in accord with a metallocyclopropane structure as occurs in the related species [(triphos)Ir{η^3-$S(Me)CH{=}CHCH{=}CH_2$}]BPh_4[25] and [$Ir(PMe_3)_3$(η^3-*C,C,S*-$SCH{=}CHCH{=}CH_2$)],[34] for which X-ray structures are available.

At this point, two relevant chemical properties of **11** and **12** need to be highlighted. First, the hydride **11** appreciably transforms into **12** only at high temperature (at 66 °C in THF, $t_{1/2}$ is 7 h). Second, neither **11** nor **12** react with H_2 under the conditions employed to hydrogenate **3a** or **3b** (compare Schemes 3 and 6). Only by addition of a proton from $HBF_4{\cdot}OEt_2$ to **12** is the resulting species, [(triphos)Ir(η^4-$S(C_6H_4)C(H)Me$)]BF_4 (**13c**) isolated as red crystals, capable of reacting with H_2 to give the thiolate dimer [(triphos)IrH(μ-*o*-$S(C_6H_4)C_2H_5)_2$HIr(triphos)]$(BF_4)_2$ (**9c**) (see below). Interestingly, the hydrogenation of **13c** to **9c** rapidly occurs also at 1 atm of H_2, a pressure which is not sufficient to accomplish the hydrogenation of the iridabenzothiabenzene precursor.

The proton added to **12** is selectively delivered to C_2 that consequently becomes a methyl carbon. The regiospecificity of the H^+ addition was confirmed by labeling studies with the use of $DOSO_2CF_3$. The $S(C_6H_4)C(H)Me$ ligand in **13c** thus binds iridium through the C_3 carbon atom (δC_3 58.7, $^2J(C_3P)$ = 17.5 Hz) and the sulfur. Even so, however, the metal center would be electronically unsaturated (16-electron species). Accordingly, we suggest an η^4-*C,C',C'',S* pseudodienic bonding mode as shown in Scheme 5. The participation of a double bond from the arene moiety in bonding the metal center, even though new for BT chemistry, has several related precedents in the literature, particularly in the reactions of vinylarenes with transition metals.[36] The structural formulation proposed for **13c** is supported by a variable-temperature ^{31}P NMR study[37] and definitely demonstrated by the subsequent reaction of **13c** with H^- to give the stereochemically rigid complex [(triphos)IrH(η^2-$S(C_6H_4)C(H)Me$)] (**14**).

Complex **14** is isolated as sandy crystals. The hydride coordinates (δH −10.00; ν(Ir–H) 2132 cm^{-1}) trans to a phosphorus donor (^2J(HP) = 176.2 Hz) and thus increases the electron density at the metal center. As a result, iridium can bind the $S(C_6H_4)CHMe$ ligand only through the sulfur and the C_3 atom which, in fact, exhibits a significant high-field shift (from 58.7 to 33.0 ppm) and a larger coupling to the trans phosphorus [$^2J(C_3P)$ = 69.9 Hz] as compared to the analogous nucleus in **13c**.

Finally, **14** reacts with either H_2 (20 °C, 5 atm) or H^+ from $HBF_4{\cdot}OEt_2$ to give **8** and the dimer **9c**, respectively.

As mentioned above, **13c** in THF reacts with 1 atm of H_2, converting to the dimer **9c**. Analogously, the tetraphenylborate salt of $\mathbf{9^{2+}}$, namely [(triphos)IrH{μ-*o*-$S(C_6H_4)C_2H_5$}$_2$HIr(triphos)]$(BPh_4)_2$ (**9a**), is obtained by treatment of [(triphos)Ir(η^4-$S(C_6H_4)C(H)Me$)]BPh_4 (**13a**) in CH_2Cl_2 at room temperature with 1 atm of H_2 (Scheme 6). In contrast, **13a** in THF reacts with H_2 (1 atm) at 20 °C to give **8**, BPh_3, and C_6H_6. From a perusal of the results summarized in Scheme 6, it is therefore evident that the formation of the neutral species **8** from [(triphos)Ir(η^4-$S(C_6H_4)C(H)Me$)]$^+$ ($\mathbf{13^+}$) requires the use of THF as solvent and of BPh_4^- as counteranion. It is also worth stressing that, irrespective of the solvent and counteranion, the hydrogenation of [(triphos)Ir(η^4-$S(C_6H_4)C(H)Me$)]$^+$ occurs at a lower hydrogen pressure than is required to hydrogenate the starting iridabenzothiabenzene complex (5 atm).

Discussion

Coordination and Opening of BT. The availability of a 14-electron system such as [(triphos)Ir]$^+$ generated in situ by thermal elimination of benzene from $\mathbf{1^+}$ has allowed the isolation and characterization of complex $\mathbf{2^+}$ containing an unprecedented η^3-*C,C',S* bonding mode of BT. A closely related bonding mode has been suggested to be involved in the so-called three-point mechanism for the heterogeneous HDS of thiophenic molecules.[39a]

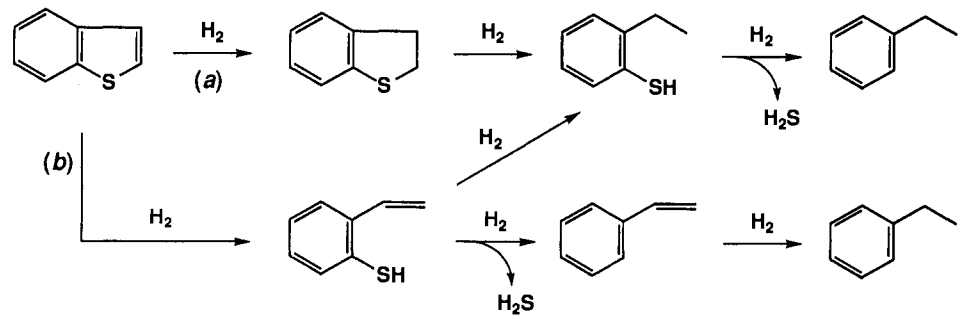
The potential of BT to act as an η^3-ligand through the sulfur and the C_2–C_3 double bond has previously been suggested. By using the 16-electron fragment $Cp'(CO)_2Re$ (Cp' = Cp or Cp*), Angelici has shown that BT coordinates in $Cp'(CO)_2ReBT$ as a mixture of η^1-*S* or 2,3-η^2-*C,C* isomers in an equilibrium concentration, depending on the electron density on the metal center.[7b,c] The contemporaneous coordination through the sulfur and the 2,3-olefin bond has been observed only in bimetallic species obtained by reacting $Cp'(CO)_2ReBT$ with $W(CO)_5(THF)$.[7b]

All the other known BT metal complexes generally exhibit either η^1-S (16-electron systems)[7] or η^6-arene anchoring modes (12-electron systems).[5] There is also an example of η^4-arene coordination obtained by two-electron reduction of an η^6-arene complex.[6b] It is therefore reasonable to conclude that the achievement of the important η^3-*C,C',S* bonding mode of BT requires the use of a d^8 ML_3 fragment. The adjective "important" is not misused in this case as no cleavage of BT has been observed so far, starting from isolated η^1-*S*, η^2-*C,C*, η^4-BT, or η^6-BT complexes. In contrast, the insertion of iridium into the unsubstituted C–S bond away from the aromatic ring readily occurs when a solution of $\mathbf{2^+}$ is gently heated above 40 °C. The C–S bond scission thus occurs as a low-energy thermal step. The most straightforward interpretation of this fact is to think of the η^3-BT ligand as a highly strained structure, which is also suggested by the ^{1}H and ^{13}C NMR data relative to the C_2H_2 and C_3H_3 groups. If so, a small amount of thermal energy would be sufficient to induce a rearrangement of the geometric and electronic structures of the complex and ultimately result in an electron transfer from iridium to the $\sigma^*(C_2\text{–}S)$ orbital. Indeed, the C–S bond cleavage reaction involves an oxidative addition step as the iridium center changes its formal oxidation state from +1 in $\mathbf{2^+}$ to +3 in $\mathbf{3^+}$, as shown by electrochemical studies.[40]

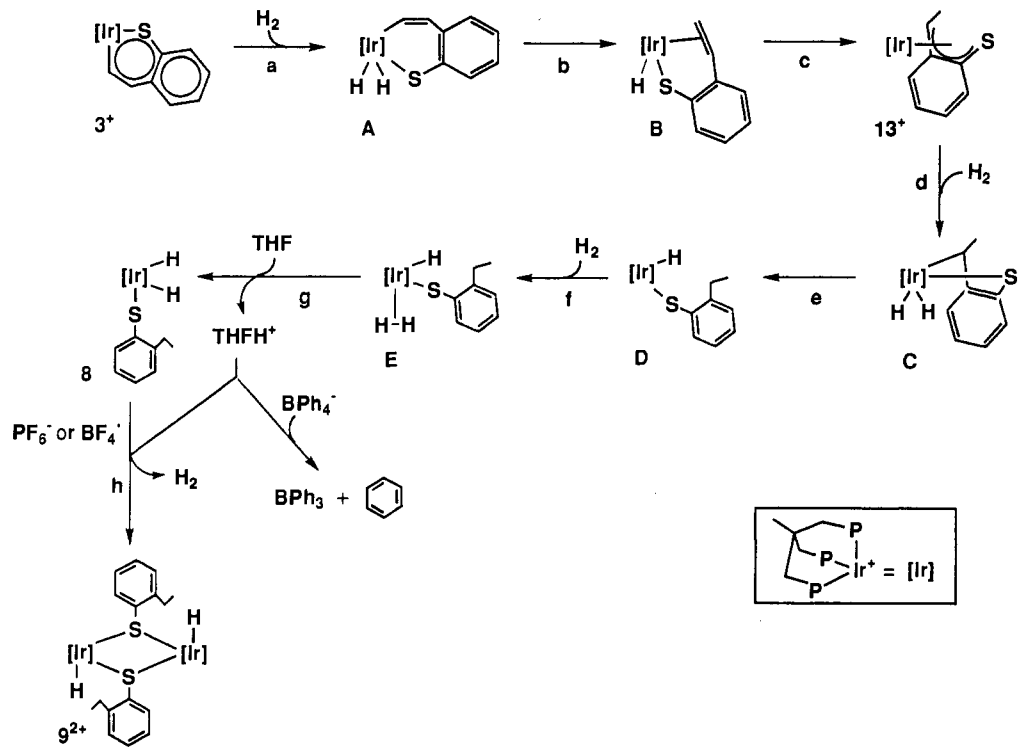
Very few examples of metal-promoted cleavages of BT in fluid solution-phase systems have been reported in the literature. Aside from Rauchfuss' benzothiaferrole $Fe_2(C_8H_6S)(CO)_6$, prepared

(35) Chen, J.; Daniels, L. M.; Angelici, R. J. *Polyhedron* **1990**, *9*, 1883.
(36) (a) Werner, H.; Feser, R. *J. Organomet. Chem.* **1982**, *232*, 351. (b) Westcott, S. A.; Marder, T. B.; Baker, R. T. *Organometallics* **1993**, *12*, 975.
(37) Compound **13c** is fluxional in solution. At room temperature the ^{31}P{^{1}H} NMR spectrum consists of an A_3 spin system. As the temperature is decreased to −10 °C, the spin system changes from A_3 to AM_2 with no discernible J(PP) couplings. The complex becomes stereochemically rigid at −70 °C, showing a well-resolved AMQ pattern. Interestingly, (i) the fluxionality involves only the phosphine ligands and not the $S(C_6H_4)CHMe$ ligand which, in fact, shows temperature-invariant chemical shifts of its carbon and hydrogen atoms, and (ii) the complex exhibits a significant temperature dependence of the phosphorus chemical shifts in the slow exchange regime (from −10 to −70 °C). This situation is quite common for d^8 MP_3(diene) complexes, particularly in the case of dienes bearing different substituents on the olefinic ends.[5] It is generally agreed that no motion other than rotation of the diene can make the three phosphorus donors equivalent.[38] This is certainly reasonable for **13c** itself where the three phosphorus donors are constrained to be part of a tridentate phosphine.
(38) Chardon, C.; Eisenstein, O.; Johnson, T.; Caulton, K. G. *New. J. Chem.* **1992**, *16*, 781.
(39) (a) Kwart, H.; Schuit, G. C. A.; Gates, B. C. *J. Catal.* **1980**, *61*, 128. (b) Singhal, G. H.; Espino, R. L.; Sobel, J. A. *J. Catal.* **1981**, *67*, 446. (c) López, R.; Peter, D.; Zdrazil, M. *Collect. Czech. Chem. Commun.* **1981**, *46*, 2185. (d) Girgis, M. J.; Gates, B. C. *Ind. Eng. Chem. Res.* **1991**, *30*, 2021. (e) Lipsch, J. M. J. F.; Schuit, G. C. A. *J. Catal.* **1969**, *15*, 179. (f) Devanneaux, J.; Maurin, J. *J. Catal.* **1981**, *69*, 202.
(40) Compound $\mathbf{3^+}$ in dichloromethane solution can reversibly be reduced to the paramagnetic Ir(II) complex [(triphos)Ir(η^2-*C,S*-C_8H_6S)] at $E^{0'}$ = −1.04 V at 20 °C: Bianchini, C.; Meli, A.; Zanello, P. Manuscript in preparation.

Scheme 7



Scheme 8. Suggested Mechanism for the Hydrogenation of 3^+ to **8** and 9^{2+} in THF at 20 °C



by the reaction of $Fe_3(CO)_{12}$ with BT,[12a] only two well-documented mononuclear complexes have been described, namely Cp*Rh(PMe$_3$)(SC$_8$H$_6$) by Jones[8] and (PMe$_3$)$_3$Ir(SC$_8$H$_6$)Cl by Merola.[11] In both cases, the metal fragment interacting with BT is a 16-electron species. On the basis of selectivity studies, Jones proposed the occurrence of η^1-*S* coordination prior to C–S bond cleavage.[41] While the intermediacy of an η^1-*S* BT ligand is chemically sound, given the 16-electron character of the metal reactant, the following insertion step is still rather obscure from a mechanistic viewpoint.

It is possible that the common transition state that all of these systems go through involves an η^2-*C,S* structure. In the case at hand, the η^2-*C,S* anchoring mode of BT would easily be accessible from the η^3-*C,C',S* structure.

Hydrogenation of BT to 2-Ethylbenzenethiol. The mechanism of HDS of BT over solid catalysts has been a subject of debate over the years.[39a,b] One of the most widely accepted proposals involves the selective hydrogenation to DHBT prior to desulfurization to yield ethylbenzene (Scheme 7, path a),[39c,d] whereas some authors prefer to view this process via initial C–S bond scission, followed by hydrogenation of the cleaved BT molecule (Scheme 7, path b).[39e,f]

Indeed, some examples of homogeneous hydrogenation of BT to DHBT have recently been reported, and catalytic cycles have also been suggested.[9,10] In no case, however, was the hydrogenation of BT to DHBT followed by its opening or desulfurization.

In contrast, as is evident from a comparison of the reactions shown in Schemes 2 and 3, the hydrogenation of BT at the [(triphos)Ir]$^+$ system occurs after and not prior to insertion of the metal into the S–C$_2$ bond. This evidence assumes a particular relevance as one realizes that the [(triphos)Ir]$^+$ fragment might promote the hydrogenation of BT to DHBT, provided the unfastening of the sulfur atom in 2^+ is possible. In this case, the system [(triphos)Ir(η^2-*C,C'*-BT)]$^+$ would appropriately be designed to oxidatively add H_2 and, ultimately, assist the hydrogenation of the double bond.[30] The fact that this reaction does not occur is ascribed to the great affinity of both [(triphos)Ir(H)$_2$]$^+$ and [(triphos)Ir]$^+$ for sulfur coordination (Scheme 2). Indeed, the sulfur atom of BT strongly coordinates iridium, as shown also by the constant sulfur coordination along the stepwise transformation of 3^+ to either **8** or 9^{2+} (Scheme 5). Strong sulfur coordination by the catalyst may thus be a requisite for HDS of BT proceeding via ring opening prior to hydrogenation.

Incorporation of all the above experimental evidence leads to several mechanistic conclusions for the homogeneous hydrogenation of 3^+ in THF, some of which are summarized in Scheme 8.

First of all, it is evident that neither **11** nor **12** is an intermediate species along the hydrogenation reaction. Neither compound, in fact, reacts with H_2 in our experimental conditions. Conversely, the complex cation [(triphos)Ir(η^4-S(C$_6$H$_4$)C(H)Me)]$^+$ (13^+) is a probable intermediate, as it readily reacts with H_2 to give either **8** or 9^{2+}, depending on the nature of the counteranion.

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

Angelici has shown that the iridathiabenzene complex Cp*Ir(η^2-*C*,*S*-2,5-Me_2T) undergoes oxidative addition of H_2 to give Cp*Ir(η^2-*C*,*S*-2,5-Me_2T)$(H)_2$.[35] In view of this report, it is reasonable to propose the occurrence of an analogous reaction step when 1 equiv of H_2 is added to $\mathbf{3}^+$ (step a) to give the dihydride [(triphos)Ir(η^2-*C*,*S*-C_8H_6S)$(H)_2$]$^+$ (**A**). From the latter compound, the formation of $\mathbf{13}^+$ may formally be described as a sequential migration of two hydrogen atoms from the metal to the C_2 carbon atom of the opened BT. In particular, the conversion of **A** to $\mathbf{13}^+$ is likely traversed by a reductive elimination step to give complex **B**, which, although not detected, is a reasonable intermediate in the independent protonation reaction of **12** yielding $\mathbf{13}^+$ (Scheme 5).[42] In a similar manner, oxidative addition of H_2 (step d), followed by hydride migration onto the CH(Me) carbon (step e), would transform $\mathbf{13}^+$ into the electronically and coordinatively unsaturated fragment [(triphos)Ir(H){S(C_6H_4)-C_2H_5}]$^+$ (**D**). From the latter species, $\mathbf{9}^{2+}$ is finally obtained when the counterion is either PF_6^- or BF_4^-. Conversely, in the presence of BPh_4^- anions in THF, the hydrogenation of $\mathbf{13}^+$ yields **8**, BPh_3, and C_6H_6. This result is consistent with a proton abstraction by THF at a certain stage of the hydrogenation, followed by reaction of protonated THF with BPh_4^- to give BPh_3 and benzene.[45] Formally this process corresponds to a heterolytic splitting of H_2.

The heterolytic cleavage of H_2 mediated by transition-metal complexes is a well-known process that may occur in either intramolecular or intermolecular fashion and is generally assisted by a base.[46,47] In light of the recent discovery of the ubiquitous nature of η^2-H_2 metal complexes, as well as detailed studies on their chemistry, it is now agreed that a number of previously observed heterolytic splittings of H_2 do involve the intermediacy of η^2-H_2 ligands.[43] These, in fact, are acidic in nature[47] and can be deprotonated even by ethers.[48] On the basis of the results presented in Scheme 6, the formation of an η^2-H_2 complex capable of reacting with THF/BPh_4^- most likely occurs at step f (reaction of intermediate **D** with H_2). In fact, were an η^2-H_2 complex formed at step d, the resulting [(triphos)Ir(η^2-S(C_6H_4)C(H)-Me)(H_2)]$^+$ species would be deprotonated by THF/BPh_4^- to give **14** (Scheme 5). However, the latter complex is stable under 1 atm of H_2 and thus should be the termination product of the reaction between $\mathbf{13}^+$ and 1 atm of H_2, which in fact is not observed (Scheme 6). Accordingly, we think that only intermediate **D** may form an η^2-H_2 complex (**E**), which is converted to **8** in the presence of BPh_4^-. In the presence of PF_6^- or BF_4^-, the proton abstracted by THF is not neutralized by the counterion and thus can react with **8** to give H_2 and either **9b** or **9c** (step h), as shown by the independent reaction of **8** in THF with HBF_4·OEt_2 (Scheme 5). The active role of THF in the hydrogenation of **13a** to **8** is demonstrated by the analogous reaction performed in CH_2Cl_2, which selectively gives **9a**. In this case, the weakly bound η^2-H_2 ligand remains intact and thus can easily be eliminated in the course of the dimerization process to $\mathbf{9}^{2+}$.

It is worth commenting that the overall hydrogenation of $\mathbf{3}^+$ to either **8** or $\mathbf{9}^{2+}$ requires the use of 5 atm of H_2, whereas the independent hydrogenation of $\mathbf{13}^+$ can be accomplished with 1 atm of H_2. This result, which also suggests step a as the rate-determining step of the overall hydrogenation, is not surprising in view of the pseudoaromaticity of $\mathbf{3}^+$.

The pathway for hydrogenation of BT to give the 2-ethylbenzenethiolate ligand involes a number of steps (C–S insertion/H_2 oxidative addition/vinyl group reductive elimination/olefin insertion/alkyl hydride reductive elimination) that have recently been proposed by Jones et al. for the desulfurization of thiophene by the dimer $[(C_5H_5)IrH_3]_2$.[49]

Conclusion

In conclusion, an unforeseen η^3-*C*,*C*′,*S* coordination of BT to a transition-metal center active in HDS has been observed. This bonding mode activates BT in such a way that insertion of the metal into the unsaturated C–S bond away from the aromatic ring occurs as a low-energy thermal step.

The hydrogenation of BT at the [(triphos)Ir]$^+$ system takes place after and not prior to C–S bond cleavage.

With the combination of a polyphosphine ligand and of a kinetically sluggish third-row transition metal, we have been able to detect several species potentially intermediate in the hydrogenation of the η^2-*C*,*S*-C_8H_6S complex. Among the various intermediates, particularly important is the product obtained by uptake of the first H_2 molecule as two hydrogen atoms are delivered to the C_2 carbon atom, a reaction path which has never been observed.

Even though one cannot exclude the occurrence of heterolytic cleavages of H_2 along the transformation of the η^2-*C*,*S*-C_8H_6S ligand to η^1-S(C_6H_4)C_2H_5, a reaction of this type does occur in the THF-assisted rearrangement of η^1-S(C_6H_4)C_2H_5 to μ-S-(C_6H_4)C_2H_5. However, this process is marginal with respect to the hydrogenation of BT at iridium.

Finally, the 2-ethylbenzenethiolate ligand can be removed as 2-ethylbenzenethiol by acidolysis with HCl.

Acknowledgment. Thanks are due to Mr. Dante Masi for collecting X-ray data. A Graduate Fellowship from CONICIT (Caracas) to V.H. for an exchange visit to the ISSECC (Firenze) is gratefully acknowledged.

Supplementary Material Available: Tables of positional and thermal parameters, and anisotropic *U* values for **3a**·1.5THF·0.5EtOH (5 pages); listing of observed and calculated structure factors for **3a**·1.5THF·0.5EtOH (43 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(42) Alternative to this mechanism is the initial formation of an η^2-H_2 complex of the formula [(triphos)Ir(η^2-*C*,*S*-C_8H_6S)(H_2)]$^+$. In fact, both the oxidation state and the coordination number of the metal center in $\mathbf{3}^+$ are appropriate for the formation of an η^2-H_2 complex.[43] From the latter complex, intermediate **B** may simply form via intermolecular acid–base interaction between the acidic η^2-H_2 (vide infra) and the basic vinyl ligand.[44]

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