Opening, Desulfurization, and Hydrogenation of Thiophene at Iridium. An Experimental Study in a Homogeneous Phase

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Abstract: The η^4-benzene complex $[(triphos)Ir(C_6H_6)]BPh_4$ reacts with thiophene to give the iridathiabenzene complex $[(triphos)Ir(\eta^2\text{-}C,S\text{-}C_4H_4S)]BPh_4$ (**1**) [triphos = $MeC(CH_2PPh_2)_3$]. Compound **1** is selectively converted to the butadienethiolate complex $[(triphos)Ir(\eta^3\text{-}SCH{=}CHCH{=}CH_2)]$ (**2**) by reaction with $LiHBEt_3$ via the (thiapentadienyl)-hydride kinetic intermediate $[(triphos)IrH(\eta^2\text{-}C,S\text{-}C_4H_4S)]$ (**3**). Compound **2** is straightforwardly obtained by reaction of $[(triphos)Ir(H)_2(C_2H_5)]$ with thiophene. This reaction produces also the (2-thienyl)dihydride $[(triphos)Ir(H)_2\text{-}(2\text{-}C_4H_3S)]$ (**4**) through a parallel C–H bond activation path. The thienyl complex is not a kinetic intermediate for the opening reaction of thiophene. Compound **2** reacts with $HBF_4{\cdot}OEt_2$ in the presence of CO yielding the thiocrotonaldehyde complex $[(triphos)Ir(CO)\{\eta^4\text{-}S{=}CHCH{=}CH(Me)\}]BF_4$ (**5**) and with PhSH to give the allylthioaldehyde derivative $[(triphos)Ir(SPh)(\eta^4\text{-}S{=}CHCH_2CH{=}CH_2)]$ (**6**). The latter compound is stable in the solid state, but re-forms **2** and PhSH in solution unless an excess of thiophenol is added. Stirring **2** with a 5-fold excess of HCl produces the trichloride $[(triphos)IrCl_3]$, H_2S, $CH_2{=}CHCH{=}CH_2$, $CH_2{=}CHCH_2CH_2SH$, and $CH_3CH_2\text{-}CH{=}CHSH$. Methylation of **2** with MeI, followed by $NaBPh_4$ addition, gives the methyl buta-1,3-dienyl thioether complex $[(triphos)Ir\{\eta^3\text{-}S(Me)CH{=}CHCH{=}CH_2\}]BPh_4{\cdot}0.5EtOH$ (**8**) which has been characterized by a single-crystal X-ray analysis. Compound **8** crystallizes in the space group $P2_1/n$. The coordination geometry around the iridium center is a distorted octahedron. The phosphorus atoms of triphos occupy three *fac* positions of the coordination polyhedron. The coordination of the metal fragment is completed by the thioether ligand which uses the sulfur atom and the two carbon atoms of the distal olefinic moiety to bind the metal. Compound **8** reacts with gaseous HCl converting to $[(triphos)IrCl_3]$ and evolving $CH_2{=}CHCH_2CH_2SMe$ and $CH_3CH_2CH{=}CHSMe$. Treatment of **8** with $THF{\cdot}BH_3$, followed by ROH addition (R = Me, Et), gives $[(triphos)IrH(SMe)(ROH)]BPh_4$ (R = Me, **9**; Et, **10**) and buta-1,3-diene. All reactions have been carried out in tetrahydrofuran.

Introduction

Heterogeneous hydrodesulfurization (HDS), the catalytic process which is used to remove sulfur from organosulfur compounds in fossil fuel feedstocks by reaction with hydrogen, is being practiced on immense industrial scale.[1] Due to the commercial importance of this process, a tremendous number of surface science and reactor studies have been directed toward elucidating its molecular mechanism, especially for thiophene derivatives.[2] In fact, thiophenic compounds represent the most abundant and refractory class of sulfur-containing organics in heavy petroleum fractions and coal-derived liquids.[3] Owing to the complexity of the heterogeneous system and in spite of many efforts, most aspects of the HDS mechanism are still debated. In particular, there is no consensus on the initial binding mode of thiophenes to the metal sites on the catalyst surface (via S-atom[4] only, as a π complex involving the diene moiety[5] or via the entire π-system in an η^5-fashion)[6] and on the desulfurization pathway which follows adsorption (does C–S bond cleavage occur after[7] or prior[8] to thiophene hydrogenation?).

Homogeneous reactions of thiophenes with transition metals constitute a recent modeling approach for elucidating the HDS mechanism.[9] A variety of coordination modes of thiophene have been authenticated or proposed (η^5, η^4, 2,3-η^2, $\eta^1(S)$, $\eta^1(C)$, and C,S)[10,11] and some reactions in which the ring has been cleaved[12] or desulfurized[12a,13] by transition metal complexes have been reported. Also, the rupture of the C-S bond of coordinated thiophenes upon reaction with hydride or other nucleophiles has

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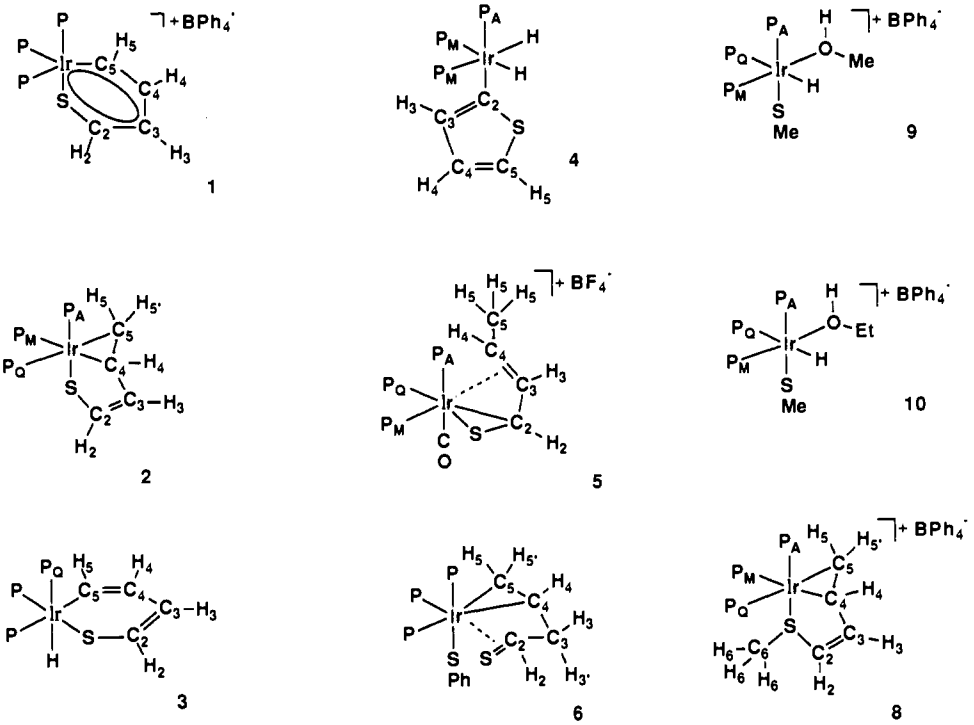
Chart I



been observed.[14] In contrast, very little is known on the reactivity of coordinated thiophenes in both the intact and open form.

Recently, we have found that the 14-e⁻ [(triphos)Ir]⁺ fragment is able to coordinate a benzene molecule in η^4 fashion[15] and then to assist its stepwise reduction to cyclohexene.[16] Intrigued by this finding and by the fact that iridium is one of the most active HDS metals,[4b,17] it seemed interesting to probe the potential of the [(triphos)Ir]⁺ moiety as the homogeneous model in the HDS of thiophene.

In this paper we report evidence for thiophene ring opening by iridium to give the iridathiabenzene complex [(triphos)Ir(η^2-*C,S*-C_4H_4S)]BPh_4 (**1**).

The possible occurrence of *C,S* coordination of thiophenes to the metal sites on the heterogeneous catalysts in the HDS process[4a] along with the relative scarcity of investigations on the reactivity of the open C_4H_4S fragment[18] prompted us to investigate the behavior of **1** toward sequential addition of H^- and electrophiles, such as HCl, PhSH, MeI, and BH_3, thereby to explore whether or not *C,S*-bonded thiophene is activated to react in a manner which may account for the reactivity of thiophene on HDS catalysts. In fact, both hydride[17b,19] and proton sources are supposed to be available on the surface of the HDS catalyst.[9,20]

Our observation of some unprecedented hydrogenation and cleavage reactions of thiophene, hopefully, will contribute to a better understanding of metal-assisted thiophene activation at the molecular level.

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 $LiAlH_4$, CH_2Cl_2 from P_2O_5, and *n*-heptane from sodium. The solvents were stored over molecular sieves and purged with nitrogen prior to use. Commercial thiophene (Aldrich, 99%) was purified as described previously.[21] The borane–tetrahydrofuran complex ($THF{\cdot}BH_3$, 1.0 M solution in THF), $LiHBEt_3$ (1.0 M solution in THF), 2-thienyllithium (2-LiC_4H_3S, 1.0 M solution in THF), and $HBF_4{\cdot}OEt_2$ (85% solution in OEt_2) were purchased from Aldrich Chemical Co. All other chemicals were commercial products and were used as received without further purifications. Literature methods were used for the preparation of [(triphos)Ir(C_6H_6)]BPh_4,[15] [(triphos)Ir$(H)_2(C_2H_5)$],[22] and [(triphos)-Ir$(H)_2$(THF)]BPh_4.[16] The solid 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 spectrometer using samples mulled in Nujol between KBr plates. Deuterated solvents for NMR measurements were dried over molecular sieves. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded either on a Varian VXR 300 (299.94 and 75.43 MHz) or a Bruker ACP 200 (200.13 and 50.32 MHz) spectrometer. ^1H NMR shifts were measured relative to residual ^1H resonances in the deuterated solvents:

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CD_2Cl_2 (δ 5.32) and THF-d_8 (δ 1.87). $^{13}C\{^1H\}$ NMR were measured relative to the deuterated solvent resonance (CD_2Cl_2, δ 53.1; C_6D_6, δ 128.0). $^{31}P\{^1H\}$ NMR spectra were recorded on the same instruments 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. The line-shape analysis of the variable-temperature NMR spectra was accomplished by means of the DNMR3 program[23] adapted for a Compaq Deskpro 386/25 personal computer. 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 with that used for GC analyses.

Synthesis of [(triphos)Ir(η²-*C*,*S*-C_4H_4S)]BPh_4 (1). A solution of [(triphos)Ir(C_6H_6)]BPh_4 (1.21 g, 1.0 mmol) and thiophene (1.57 mL, 20 mmol) in THF (40 mL) was kept at 40 °C for 6 days during which time the color of the solution changed gradually from yellow orange to orange red. Quantitative formation of benzene was detected by GC. After evaporation of the solvent under vacuum, the residue was dissolved with CH_2Cl_2 (30 mL). Addition of ethanol (50 mL) and slow concentration under a steady stream of nitrogen led to the precipitation of brick red crystals, which were washed with ethanol and *n*-pentane; yield 90%. Anal. Calcd for $C_{69}H_{63}BIrP_3S$: C, 67.92; H, 5.20; Ir, 15.75; S, 2.63. Found: C, 67.83; H, 5.19; Ir, 15.55; S, 2.48. Λ_M: 52 Ω^{-1} cm^2 mol^{-1}.

Synthesis of [(triphos)Ir(η³-SCH=CHCH=CH_2)] (2). A solution of **1** (0.20 g, 0.16 mmol) in THF (20 mL) at room temperature was treated with a 4-fold excess of $LiHBEt_3$ (0.64 mL, 0.64 mmol). There was an immediate color change from red to yellow. The reaction solution was then kept at approximately 50 °C for ca. 1 h. After destroying the excess of $LiHBEt_3$ with ethanol (5 mL), addition of *n*-heptane (20 mL) and slow concentration gave yellow crystals which were washed with *n*-pentane; yield ca. 85%. Anal. Calcd for $C_{45}H_{44}IrP_3S$: C, 59.92; H, 4.92; Ir, 21.31; S, 3.55. Found: C, 60.03; H, 5.03; Ir, 20.89; S, 3.38. IR: ν(C=C) 1550 (m) cm^{-1}.

Reaction of 1 with $LiHBEt_3$. (A) NMR Experiment. About 30 mg (0.02 mmol) of **1** was dissolved in 0.7 mL of THF-d_8 and placed in an NMR tube under nitrogen. The solution was frozen with liquid nitrogen and a 4-fold excess of $LiHBEt_3$ (0.08 mL, 0.08 mmol) was syringed into the tube which was then kept at −50 °C for 30 min. The $^{31}P\{^1H\}$ NMR spectrum of this sample, recorded at −50 °C, indicated the complete conversion of **1** to a new product displaying an AMQ spin system. This product is thermally unstable slowly converting to **2** at higher temperature; complete transformation was achieved upon warming at 50 °C for ca. 1 h.

(B) Synthetic Experiment. To a red orange solution of **1** (0.20 g, 0.16 mmol) in THF (20 mL) at approximately −50 °C was added a 4-fold excess of $LiHBEt_3$ (0.64 mL, 0.64 mmol). Immediately the solution became yellow in color. The volatiles were then removed at 0 °C in vacuo and the residue, washed with ethanol (3 × 5 mL) and *n*-pentane, gave a yellow microcrystalline solid; yield 70%. This product was shown to be a mixture of **2** (10–30%) and a new compound which was characterized by IR and NMR spectroscopy as [(triphos)IrH(η²-*C*,*S*-C_4H_4S)] (**3**). Its $^{31}P\{^1H\}$ NMR spectrum, recorded at −50 °C, matched that of the intermediate observed during the above NMR experiment. IR: ν(Ir–H) 2086 (m) cm^{-1}.

Reaction of [(triphos)Ir(H)₂(C_2H_5)] with Thiophene. (A) NMR Experiment. A 5-mm NMR tube was charged with a mixture of [(triphos)Ir(H)₂(C_2H_5)] (25 mg, 0.03 mmol) and thiophene (48 μL, 0.60 mmol) in THF-d_8 (0.7 mL) under nitrogen, flame-sealed, and placed in a NMR spectrometer at 70 °C. ^{31}P and ^1H NMR spectra were recorded every hour. Besides the starting complex, two other products were observed in a ratio of ca. 6:1 just in the first spectrum. The major product was identified as **2** and the second product was identified as the C–H bond activation product [(triphos)Ir(H)₂(2-C_4H_3S)] (**4**) by comparison with an authentic sample (see below). No evidence of other species was observed. After 4 h, only **2** and **4** were present in solution in the same ratio. After an additional 12 h, NMR integration revealed no change in the product composition, thus suggesting that **2** and **4** are formed by parallel reactions rather than sequential ones.

(B) Synthetic Experiment. To a suspension of [(triphos)Ir(H)₂(C_2H_5)] (0.50 g, 0.59 mmol) in THF (40 mL) was added a 20-fold excess of thiophene (0.95 mL, 11.90 mmol) and then the mixture was heated at reflux temperature. Within a few minutes the solid dissolved to give a bright yellow solution. After ca. 4 h the solution was allowed to reach room temperature. Both **2** (ca. 85%) and **4** (ca. 15%) were identified in the reaction mixture by ^{31}P NMR spectroscopy. The solution was eluted with *n*-heptane (20 mL), and because of the higher solubility of **4** as compared to **2**, pure samples of **2** in ca. 80% yield could be obtained.

Synthesis of [(triphos)Ir(H)₂Cl]. A mixture of [(triphos)Ir(H)₂(THF)]BPh_4 (0.30 g, 0.25 mmol) and LiCl (0.04 g, 1.00 mmol) in THF (20 mL) was stirred for 1 h at room temperature. On addition of ethanol (30 mL) and partial evaporation of the solvents off-white crystals precipitated. They were collected by filtration, washed with ethanol and *n*-pentane, and then recrystallized from THF and *n*-heptane; yield 80%. The IR and NMR data of this complex were in perfect agreement with those reported in the literature.[24]

Synthesis of [(triphos)Ir(H)₂(2-C_4H_3S)] (4). A sample of [(triphos)Ir(H)₂Cl] (0.20 g, 0.23 mmol) was dissolved in THF (30 mL) at room temperature and then a 1 M solution (0.92 mL) of 2-LiC_4H_3S in THF (0.92 mmol) was added with stirring. After 3 h the resulting red solution was concentrated to dryness and the residue treated with ethanol (5 mL). Addition of *n*-heptane (30 mL) led to the precipitation of yellow crystals, which were recrystallized twice from THF/*n*-heptane; yield 60%. Anal. Calcd for $C_{45}H_{44}IrP_3S$: C, 59.92; H, 4.92; Ir, 21.31; S, 3.55. Found: C, 59.63; H, 4.71; Ir, 21.11; S, 3.36. IR: ν(Ir – H) 2054 (m) cm^{-1}, ν(C=C) 1580 (m) cm^{-1}.

Reaction of 2 with CPh_3PF_6. Equimolar amounts of **2** and CPh_3PF_6 were mixed in CD_2Cl_2 at room temperature. After 1 h, the $^{31}P\{^1H\}$ and ^1H NMR spectra of the resulting solution indicated complete conversion of **2**. Along with some unidentified products, **1** was formed in 60% yield.

Reaction of 2 with HCl. In a 100-mL Schlenk-type flask equipped with a silicone rubber septum inlet, a THF solution of gaseous HCl (5-fold excess) was added to a stirred suspension of **2** (0.20 g, 0.22 mmol) in THF (20 mL) at room temperature. An immediate reaction took place and the yellow solid dissolved to give a red solution that quickly turned red orange. After 10 min both the gas and the liquid phases were sampled and analyzed by GC/MS: 3-butene-1-thiol (CH_2=$CHCH_2$-CH_2SH, 15%) and 1-butene-1-thiol (CH_3CH_2CH=CHSH, 4%) were detected together with H_2S and buta-1,3-diene which constituted the major products (42 and 39%, respectively). In a separate experiment hydrogen sulfide was determined gravimetrically as PbS (60–70% with respect to **2**). After evaporation of the solution under vacuum, the residue, recrystallized from CH_2Cl_2 and ethanol, gave off-white crystals of [(triphos)$IrCl_3$][24] in quantitative yield. The trichloride complex was shown by ^{31}P NMR spectroscopy to be the only phosphorus-containing iridium product at the end of the reaction. Likewise, when the reaction was followed by ^1H NMR spectroscopy the formation of H_2S was shown by the appearance of a singlet at ca. 0.9 ppm. Other resonances were also present in both the aliphatic and olefinic region of the spectrum but their low intensity as well as a large overlapping of their signals also with those of the triphos ligand precluded a reliable assignment. CH_2=$CHCH_2$-CH_2SH, EIMS, 70 eV [*m*/*e* (%)]: 88 (22) M^+, 60 (31) $SC_2H_4^+$, 54 (28) $C_4H_6^+$, 47 (100) H_2CSH^+, 39 (50) $C_3H_3^+$, 24 (60) $C_2H_3^+$. CH_3CH_2-CH=CHSH, EIMS, 70 eV [*m*/*e* (%)]: 88 (29) M^+, 55 (100) M – SH^+, 54 (52) $C_4H_6^+$, 39 (53) $C_3H_3^+$, 29 (74) $C_2H_5^+$. CH_2=CHCH=CH_2, EIMS, 70 eV [*m*/*e* (%)]: 54 (57) M^+, 53 (44) $C_4H_5^+$, 39 (100) $C_3H_3^+$, 28 (26) $C_2H_4^+$, 27 (72) $C_2H_3^+$, 26 (31) $C_2H_2^+$.

Reaction of 2 with HBF_4. (A) Under Nitrogen. A 5-mm NMR tube was charged with a mixture of **2** (30 mg, 0.03 mmol) and THF-d_8 (0.7 mL) under nitrogen and cooled down to −40 °C. A stoichiometric amount of HBF_4·OEt_2 (ca. 10 μL) was then added to the suspension. An immediate reaction took place; the solid dissolved yielding a deep red solution. ^{31}P and ^1H NMR spectra of this solution recorded at −40 °C showed the quantitative conversion of **2** into a new product characterized by an AMQ spin system [δP_A −6.68, δP_M −17.68, δP_Q −45.0, $J(P_AP_M)$ = 17.8 Hz, $J(P_AP_Q)$ = 14.8 Hz, $J(P_MP_Q)$ = 5.2 Hz] as well as the absence of hydride ligands. Increasing the temperature caused decomposition of the red product. At room temperature complete conversion to several unidentified metal species occurred within 30 min.

(B) Under CO. Addition of a stoichiometric amount of HBF_4·OEt_2 (50 μL) to a suspension of **2** (0.20 g, 0.22 mmol) in THF (40 mL) under CO atmosphere (1 atm) at room temperature caused the solid to dissolve

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giving a bright red solution. After the solution was stirred for ca. 10 min, the color turned pale yellow and off-white crystals of [(triphos)Ir(CO)-{η^4-S=CHCH=CH(Me)}]BF_4 (**5**) precipitated in 70% yield. The crystals were then washed with THF and *n*-pentane. Anal. Calcd for $C_{46}H_{45}BF_4IrOP_3S$: C, 54.28; H, 4.46; Ir, 18.88; S, 3.15. Found: C, 54.13; H, 4.38; Ir, 18.71; S, 3.01. Λ_M: 84 Ω^{-1} cm^2 mol^{-1}. IR: ν(CO) 2042 (s) cm^{-1}.

Reaction of 2 with Thiophenol. Neat thiophenol (0.07 mL, 0.66 mmol) was syringed into a suspension of **2** (0.20 g, 0.22 mmol) in THF (30 mL) at room temperature. Within a few minutes the solid dissolved giving a brown yellow solution. Addition of *n*-heptane (30 mL) led to the precipitation of yellow crystals of [(triphos)Ir(SPh)(η^4-S=CHCH$_2$-CH=CH$_2$)] (**6**), which were washed with *n*-pentane; yield 80%. Anal. Calcd for $C_{51}H_{50}IrP_3S_2$: C, 60.52; H, 4.98; Ir, 18.99; S, 6.33. Found: C, 60.41; H, 4.91; Ir, 18.78; S, 6.38. IR: (reinforced phenyl absorption) 1580 (m) cm^{-1}. Monitoring a similar reaction using PhSD by ^{1}H NMR in THF-d_8 solution shows that the only resonances substantially affected are those corresponding to H_3 and $H_{3'}$ which give rise to an unresolved multiplet at 3.09 ppm. Irradiation of this resonance shows that no deuterium has been incorporated in any other carbon atom. In particular, the signal of H_2, which in the unlabeled compound appears as a doublet of doublets, becomes a complex multiplet in the deuterated complex, and a singlet upon selective decoupling of the 3.09 ppm multiplet.

Reaction of 2 with MeI. Neat MeI (0.16 mL, 2.66 mmol) was syringed into a stirred suspension of **2** (0.60 g, 0.66 mmol) in THF (30 mL) at room temperature. Within 10 min the yellow solid dissolved to give a colorless solution while off-white crystals of [(triphos)Ir{η^3-S(Me)-CH=CHCH=CH$_2$}]I (**7**) began to precipitate. Addition of *n*-heptane (10 mL) completed the precipitation; yield 85%. The crystals were then washed with a 3:1 mixture of *n*-pentane and THF and then *n*-pentane. Anal. Calcd for $C_{46}H_{47}IIrP_3S$: C, 52.92; H, 4.54; Ir, 18.41; S, 3.07. Found: C, 52.83; H, 4.49; Ir, 18.25; S, 2.95. Λ_M: 79 Ω^{-1} cm^2 mol^{-1}. Metathetical reaction of **7** with $NaBPh_4$ in CH_2Cl_2 and ethanol afforded the tetraphenylborate derivative [(triphos)Ir{η^3-S(Me)CH=CH-CH=CH$_2$}]BPh_4·0.5EtOH (**8**) in 95% yield. Alternatively, **8** was obtained by a one-pot procedure by treatment of a THF solution of **2** with MeI, followed by $NaBPh_4$ addition in ethanol. Anal. Calcd for $C_{71}H_{70}BIrO_{0.5}P_3S$: C, 67.72; H, 5.60 Ir, 15.26. Found: C, 67.29; H, 5.51; Ir, 15.14. Λ_M: 54 Ω^{-1} cm^2 mol^{-1}.

Reaction of 8 with THF·BH_3. In a 50-mL Schlenk-type flask equipped with a silicone rubber septum inlet, a 4-fold excess of THF·BH_3 (0.64 mL, 0.64 mmol) was added at room temperature to a THF (15 mL) solution of **8** (0.20 g, 0.16 mmol), previously recrystallized from THF/*n*-heptane in order to eliminate the clathrated ethanol. After 1 h the reaction mixture was sampled by a syringe and GC/MS analyzed: buta-1,3-diene (80% with respect to **8**) together with traces of MeSH were the only recognizable organic products of the reaction. The solution was then eluted with methanol (30 mL) and concentrated to ca. 10 mL. The off-white microcrystalline precipitate of [(triphos)IrH(SMe)(MeOH)]-BPh_4 (**9**) was washed with ethanol and *n*-pentane; yield 50%. Anal. Calcd for $C_{67}H_{67}BIrOP_3S$: C, 66.16; H, 5.55; Ir, 15.80; S, 2.64. Found: C, 65.99; H, 5.49; Ir, 15.67; S, 2.59. Λ_M: 56 Ω^{-1} cm^2 mol^{-1}. IR: ν(Ir-H) 2120 (m) cm^{-1}. When ethanol was employed in the place of methanol, the analogous complex [(triphos)IrH(SMe)(EtOH)]BPh_4 (**10**) was recovered in comparable yield. Anal. Calcd for $C_{68}H_{69}BIrOP_3S$: C, 66.38; H, 5.65; Ir, 15.62; S, 2.61. Found, C, 66.13; H, 5.71; Ir, 15.51; S, 2.45. Λ_M: 55 Ω^{-1} cm^2 mol^{-1}. IR: ν(Ir-H) 2119 (m) cm^{-1}.

Reaction of 8 with HCl. In a 50-mL Schlenk-type flask equipped with a silicone rubber septum inlet, a THF solution of gaseous HCl (5-fold excess) was added to a solution of **8** (0.27 g, 0.19 mmol) in THF (10 mL) at room temperature. The reaction mixture was stirred for 2 h during which time an off-white precipitate of [(triphos)$IrCl_3$][24] formed; this was collected by filtration and washed with THF and *n*-pentane; yield 80%. The formation of two unsaturated sulfides, namely 3-butenyl methyl sulfide (CH_2=$CHCH_2CH_2SMe$), and 1-butenyl methyl sulfide (CH_3-CH_2CH=$CHSMe$) in a 1:2 ratio was determined by GC/MS analysis. CH_2=$CHCH_2CH_2SMe$, EIMS, 70 eV [*m/e* (%)]: 102 (24) M$^+$, 61 (100) H_2CSMe^+, 39 (22) $C_3H_3^+$, 27 (33) $C_2H_3^+$. CH_3CH_2CH=CH-SMe, 70 eV [*m/e* (%)]: 102 (67) M$^+$, 87 (16) M - Me$^+$, 55 (100) M - SMe$^+$, 54 (68) $C_4H_6^+$, 39 (51) $C_3H_3^+$, 29 (58) $C_2H_5^+$, 27 (58) $C_2H_3^+$.

X-ray Data Collection and Structure Determination of 8. Crystals suitable for an X-ray diffraction analysis were obtained by slow concentration of a CH_2Cl_2/ethanol solution of **8** maintained under nitrogen at room temperature. A summary of crystal and intensity data is reported in Table IV. A colorless parallelepiped crystal was mounted on a glass fiber on a Enraf-Nonius CAD4 automatic diffractometer. The cell parameters were determined by least-squares refinement of the setting angles 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[25] with anomalous dispersion correction taken from ref 26. Absorption correction was applied via Ψ scan with transmission factors ranging between 79.95 and 99.95. All the calculations were carried out on a DIGITAL DEC 5000/200 computer by using the SHELX76 program.[27] 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. The phenyl rings were treated as rigid bodies of D_{6h} symmetry with C–C distances fixed at 1.39 Å and calculated hydrogen atom positions (C–H = 1.08 Å). The atoms of the clathrated ethanol molecule were all treated as carbon atoms.

Results and Discussion

The preparations and the principal reactions of the complexes described in this paper are illustrated in Scheme I and II. Selected NMR spectral data are collected in Table I [^{31}P{^{1}H} NMR] and Table II [^{1}H, ^{13}C{^{1}H} NMR].

The Iridathiabenzene Complex [(triphos)Ir(η^2-*C,S*-C_4H_4S)]-BPh_4. Stirring a THF solution of the η^4-benzene complex [(triphos)Ir(η^4-C_6H_6)]BPh_4[15] with an excess of thiophene at 40 °C produces an orange red solution from which brick red crystals of [(triphos)Ir(η^2-*C,S*-C_4H_4S)]BPh_4 (**1**) are obtained in excellent yield (>90%) by addition of ethanol. In the course of the reaction quantitative production of benzene occurs (GC).

Complex **1** is fairly air-stable in both the solid state and solution even under H_2 or O_2 (1 atm).

The complex is stereochemically nonrigid on the NMR time scale in room temperature solutions as shown by the ^{31}P{^{1}H} NMR spectrum in CD_2Cl_2 which consists of a single resonance at –0.05 ppm for the three phosphorus atoms of triphos (Figure 1, left). As the temperature is decreased, the resonance becomes broader and broader until, at –80 °C, it merges into the base line. At lower temperature, decoalescence occurs and, at –90 °C, the spectrum shows two broad signals centered at –12.66 and 4.60 ppm. For a further decrease in the temperature by using a 2:1 (v:v) CD_2Cl_2/$CFCl_3$ mixture as solvent, narrowing of both signals is observed. At –110 °C, the spectrum consists of two relatively narrow signals with no discernible J(PP) at –12.19 (1P) and 4.79 (2P), thus indicating an AM_2 spin system for the slow exchange regime.

The mutual exchange mechanism that makes the three phosphorus of triphos equivalent has been studied by DNMR3 spectroscopy assuming exchange between the three configurations $P_1P_2P_3 \Leftrightarrow P_2P_1P_3 \Leftrightarrow P_3P_1P_2$. A satisfactory simulation of the variable-temperature spectra (Figure 1, right) has been obtained by using T_2 = 0.11 s and the following rate constants k (s^{-1}): 40 000 at –50 °C, 20 000 at –60 °C, 7 500 at –70 °C, 2 750 at –80 °C, 900 at –90 °C, 250 at –100 °C, and 60 at –110 °C. An Arrhenius plot of log k vs. $1/T$ results in a straight line from which the activation parameters $\Delta H^{\ddagger}$ (7.3 ± 0.1 kcal mol^{-1}), $\Delta S^{\ddagger}$ (–3.9 ± 0.4 cal K^{-1} mol^{-1}), and $\Delta G^{\ddagger}_{(193K)}$ (8.1 ± 0.2 kcal mol^{-1}) can be calculated. The low E_a value (7.9 ± 0.1 kcal mol^{-1}) is consistent with the large temperature range which separates the fast-exchange and slow-exchange limits. The $\Delta S^{\ddagger}$ value close to zero points to an ordered transition state for the intramolecular exchange of the phosphorus atoms.

The magnetic equivalence of the three phosphorus atoms in the fast exchange regime is quite frequently observed for five-coordinate triphos metal complexes and is attributed to a fast non-bond-breaking interconversion between trigonal-bipyramidal

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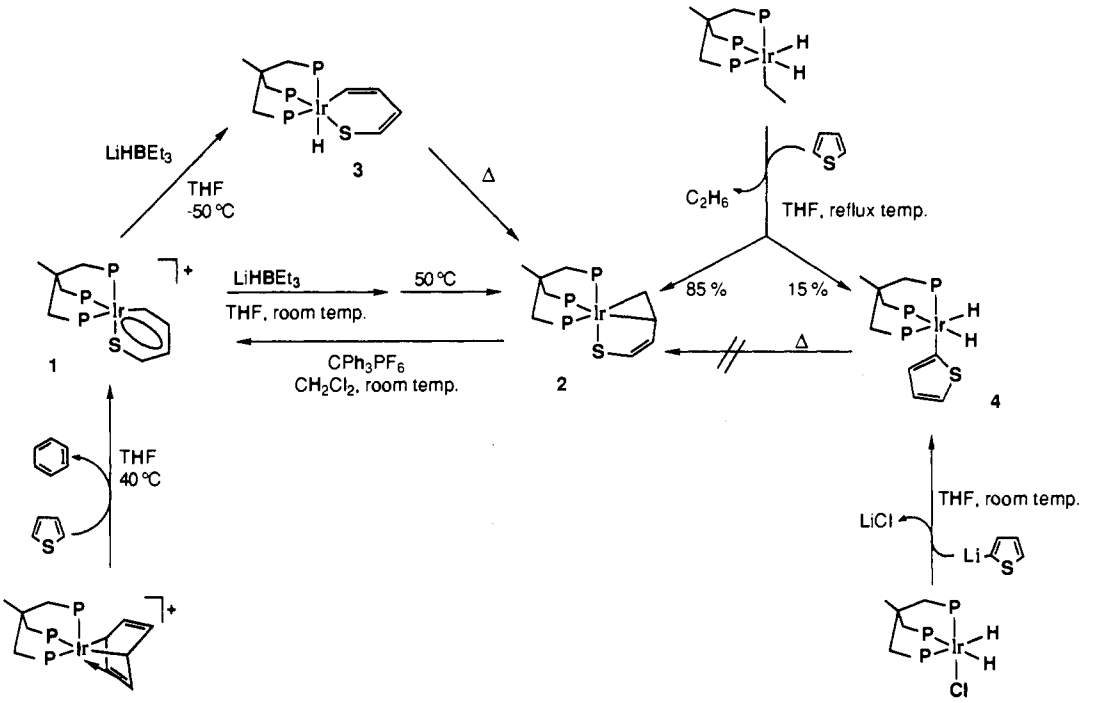
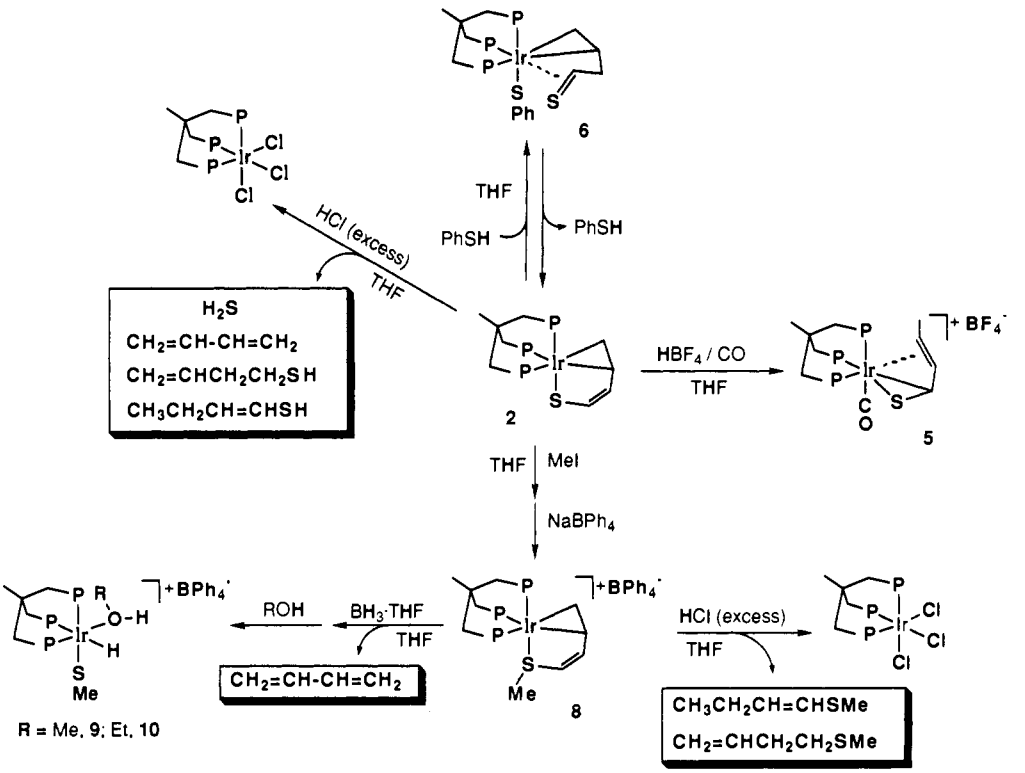
(26) *International Tables of Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4.
(27) Sheldrick, G. M. *SHELX76 Program for Crystal Structure Determinations*; University of Cambridge: Cambridge, England, 1976.

Scheme I



Scheme II



(TBP) and square-pyramidal (SP) structures.[28] Indeed, both limiting conformations have been authenticated by X-ray analyses[24,28a,29] or spectroscopic techniques.[28a,30]

On the basis of ^{31}P NMR spectroscopy only, it is not possible to discriminate between TBP and SP structures of **1**; in contrast, the ^{1}H and ^{13}C NMR data can be translated into valuable structural and chemical information. Actually, the presence of an open C_4H_4S ligand in **1** is unambiguously shown by the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra which, moreover, are quite consistent with a planar delocalized π-system,[31] i.e., iridathiabenzene ring. In fact, four distinct signals for the four methyne groups of thiophene are readily distinguishable. In particular, the positions of C_5 (δ 178.88) in the $^{13}C\{^{1}H\}$ NMR spectrum and of the methyne hydrogens (δ 9.67, 9.02, 8.38 and 8.16) in the ^{1}H NMR spectrum (Figure 2) are in the proper region of delocalized six-membered metallarings, a related example of which is contained in the related complex [Cp*Ir(η^2-2,5-Me_2T)] [2,5-Me_2T = 2,5-dimethylthiophene].[12c] The ^{1}H and ^{13}C NMR signals for the C–H atoms

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Table I. $^{31}P\{^1H\}$ NMR Spectral Data for Complexes 1–10[a]

complex	pattern	chem shift, ppm[b]			coupling const, Hz		
		$\delta(P_A)$	$\delta(P_M)$	$\delta(P_Q)$	$J(P_AP_M)$	$J(P_AP_Q)$	$J(P_MP_Q)$
1	A_3	−0.05					
1[c]	AM_2	−12.19[d]	4.79[d]				
2	AMQ	−10.70	−28.69	−32.42	21.2	16.5	32.0
3[e]	AMQ	−2.47	−31.26	−54.64	17.6	11.0	13.6
4	AM_2	−8.39	−24.11		15.5		
5	AMQ	−20.34	−30.79	−38.68	12.7	28.5	32.8
6	AMQ	−10.72	−35.45	−39.25	18.3	20.3	54.5
7/8	AMQ	−13.71	−22.39	−33.77	22.8	25.5	23.9
9	AMQ	−5.18	−24.68	−35.72	17.0	14.8	17.7
10	AMQ	−4.46	−24.49	−36.31	16.9	14.8	17.9

[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] At −110 °C in $CD_2Cl_2/CFCl_3$, 2:1 (v:v). [d] Not resolved. [e] At −50 °C in THF-d_8.

of the C_4H_4S fragment are practically temperature invariant in the range from +35 to −85 °C. At lower temperature, considerable broadening of the resonances occurs, which may be also due to a decreased homogeneity of the magnetic field. As expected, in the fast exchange regime the H and C nuclei of the metallaring look at three magnetically equivalent phosphorus nuclei (quartet substructure).

In conclusion, NMR studies support an iridathiabenzene structure for **1** in which the π-system is delocalized over the six-membered ring, thus contributing to the stability of the complex. The latter contains an iridium center in the +3 formal oxidation state, as a consequence of the oxidative addition of a C–S bond from thiophene. In this respect, we wish to briefly anticipate the results of an electrochemical study of **1** in CD_2Cl_2 solution; the complex cation undergoes a reversible (chemically and electrochemically) one-electron reduction (23 °C, $E^{\circ\prime} = -1.1$ V) to give the neutral Ir(II) derivative [(triphos)Ir(η^2-*C,S*-C_4H_4S)], which has been characterized by X-band ESR spectroscopy.[32]

Having established the presence of a C_4H_4S ligand η^2-*C,S*-bonded to Ir(III) in **1**, it is then possible to assign a TBP primary geometry to the complex cation. In fact, only a TBP structure accounts for the ^{31}P AM_2 spin system observed in the slow exchange regime (an SP structure would necessarily imply an AMQ pattern). Accordingly, the fluxionality of **1** in room temperature solutions can readily be rationalized by recalling that a d^6-ML_3 fragment has a degenerate set of empty orthogonal $d\pi$ orbitals.[28] One of these is involved in interactions of σ-type with an appropriate symmetry combination of lone pairs at the C_5 carbon and sulfur atoms of the C_4H_4S ligand. The other $d\pi$ orbital is involved in an interaction of π-type with a filled orbital delocalized over the C_4S hemicycle. Obviously, the role of the σ and π acceptor metal $d\pi$ orbitals is exchanged when the geometry rearranges from TBP to SP.

At this point, one may argue about the occurrence of an oxidative addition reaction involving a 14-electron system such as [(triphos)Ir]$^+$. Actually, a much better candidate would be a 16-electron fragment of the type [(triphos)Ir(L)]$^+$ (L = 2-electron donor). In the reaction mixture, there are at least two potential σ-donors capable of instantaneously stabilizing a 16-electron metal species: the THF solvent and thiophene itself via S-coordination. Which of the two reagents may effectively be involved in the process is hard to say since we have no spectroscopic evidence whatsoever for the formation of intermediate species in the cleavage reaction of thiophene at iridium. However, it is worth mentioning that Jones and co-workers have recently reported a case in which the oxidative addition of a C–S bond from thiophene to the [Cp*Rh(PMe_3)] fragment proceeds via an S-bonded thiophene intermediate, followed by migration of the α-carbon to the metal center.[12c,d] Also, we cannot exclude a priori that thiophene may initially coordinate the [(triphos)Ir]$^+$ fragment in η^4 fashion and then rapidly rearrange to the η^2-*C,S*-bonding mode, as shown by Angelici and co-workers for the [Cp*Ir(η^4-2,5-Me_2T)] → [Cp*Ir(η^2-2,5-Me_2T)] isomerization catalyzed by NEt_3 as well as basic Al_2O_3.[12e]

Hydride Addition to the Iridathiabenzene Complex 1. Treatment of **1** with 4 equiv of $LiHBEt_3$ in THF at room temperature, followed by heating at 50 °C for 1 h, gives complete transformation to [(triphos)Ir(η^3-SCH=CHCH=CH_2)] (**2**) by selective delivery of hydride to the C_5 carbon atom.

Compound **2** appears as stable yellow crystals in the solid state and in deoxygenated solutions in which it behaves as a nonelectrolyte. Unlike the iridathiabenzene precursor, the hydride addition product is stereochemically rigid on the NMR time scale. The $^{31}P\{^1H\}$ NMR spectrum consists of a temperature-invariant AMQ spin system and is, therefore, typical of octahedral triphos complexes containing three "different" donor atoms trans to the phosphorus atoms. ^1H and ^{13}C NMR studies unambiguously show that these three donors come from an η^3-*S,C,C*-butadienethiolate ligand which uses a terminal olefinic end and the sulfur atom to bind the metal. From a perusal of the NMR data, one can also infer that (i) the C_5 and C_4 carbon atoms are strongly bound to the metal center [$^2J(C_4P_M) = 32.9$ Hz, $^2J(C_5P_Q) = 38.5$ Hz, $^3J(H_5H_4) = {}^3J(H_{5'}H_4) = 7.4$ Hz, $^2J(H_5H_{5'}) = 1.6$ Hz], as occurs in metal–π-olefin bonds exhibiting metallacyclopropane structure,[22,33] and (ii) the π-delocalization over the metallaring has disappeared, a double bond being now localized between C_2 (δ 129) and C_3 (δ 133), as indicated also by the appearance of a ν(C=C) band at 1550 cm^{-1} in the IR spectrum. Quite similar spectroscopic properties are shown by the 5-thiapentadienyl complex [Ir(PMe_3)$_3$(η^3-*C,C,S*-SCH=CHCH=CH_2)] recently obtained by reaction of [Ir(PMe_3)$_3$Cl] with potassium thiapentadienide and authenticated by X-ray diffraction.[34]

Indirect but substantial support of the structural assignment of **2** made on the basis of NMR spectroscopy has been provided by an X-ray diffraction study of the methyl buta-1,3-dienyl thioether complex [(triphos)Ir{η^3-S(Me)CH=CHCH=CH_2}]-BPh_4·0.5EtOH (**8**). Compound **8** is quantitatively obtained by treatment of a THF solution of **2** with MeI, followed by metathetical reaction with $NaBPh_4$ in ethanol.

The structure consists of discrete [(triphos)Ir{η^3-S(Me)-CH=CHCH=CH_2}]$^+$ cations, BPh_4^- anions, and chlatrated ethanol molecules in a 1:1:0.5 ratio. An ORTEP drawing of the complex cation is shown in Figure 3. Selected bond distances and angles are reported in Table III.

The coordination geometry around the iridium center is a distorted octahedron. The phosphorus atoms of triphos occupy three *fac* positions of the coordination polyhedron, the P–Ir–P angles being only a bit less than 90°, as usual. The coordination of the metal fragment is completed by the methyl buta-1,3-dienyl thioether which uses the sulfur atom, *trans* to P_2, and the two carbon atoms (C_6, C_9) of the distal olefinic moiety. The

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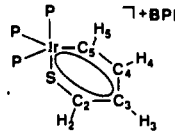
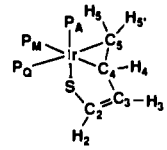
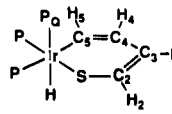
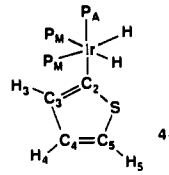
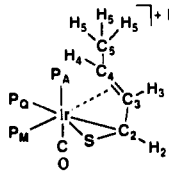
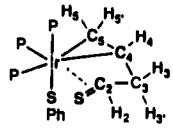
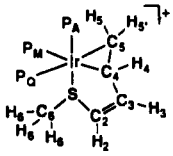
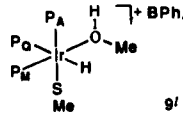
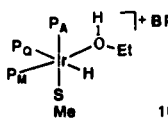
(34) Bleeke, J. R.; Ortwerth, M. F.; Chiang, M. Y. *Organometallics* **1992**, *11*, 2740.

Table II. Selected NMR Spectral Data for the Complexes **1–6** and **8–10**[a]

complex	^{1}H NMR assignt	^{1}H NMR δ (multiplicity, *J*)[b]	^{13}C{^{1}H} NMR assignt	^{13}C{^{1}H} NMR δ (multiplicity, *J*)[b]
 **1**	H_5	9.67 (dqd, $^3J(H_5H_4)$ = 10.6, $^4J(H_5H_3)$ = 0.9, $^3J(H_5P)$ = 6.5)	C_5	178.88 (q, $^2J(C_5P)$ = 22.5)
			C_3	134.05 (q, $^4J(C_3P)$ = 2.3)
	H_2	9.02 (dq, $^3J(H_2H_3)$ = 8.9, $^4J(H_2P)$ = 3.4)	C_2	131[c]
	H_3	8.38 (tm, $^3J(H_3H_4)$ = 8.0, $^5J(H_3P)$ = 1.0)	C_4	126[c]
	H_4	8.16 (qq, $^4J(H_4P)$ = 6.0)		
 **2**[d]	H_3	6.14 (q, $^3J(H_3H_2)$ = 6.1, $^3J(H_3H_4)$ = 4.8, $^4J(H_3P_M)$ = 5.3, $^4J(H_3P_A)$ = 1.0)	C_3	133[c]
			C_2	129[c]
	H_2	5.67 (td, $^4J(H_2P_A)$ = 6.3, $^4J(H_2P)$ = 2.1)	C_4	50.25 (dd, $^2J(C_4P_M)$ = 32.9, $^2J(C_4P_A)$ = 8.2)
	H_4	2.68 (m, $^3J(H_4H_5)$ = $^3J(H_4H_{5'})$ = 7.4, $^3J(H_4P_A)$ = 2.4, $^3J(H_4P_M)$ = 2.0)	C_5	25.69 (ddd, $^2J(C_5P_Q)$ = 38.5, $^2J(C_5P_A)$ = 7.3, $^2J(C_5P_M)$ = 2.9)
	H_5	2.04 (m, $^2J(H_5H_{5'})$ = 1.6, $^3J(H_5P_Q)$ = 7.5, $^3J(H_5P_A)$ = 4.8, $^3J(H_5P_M)$ = 4.0)		
	$H_{5'}$	1.67 (qt, $^3J(H_{5'}P_A)$ = $^3J(H_{5'}P_Q)$ = 7.5, $^3J(H_{5'}P_M)$ = 2.0)		
 **3**[e,f]	H_2	6.63 (br d, $^3J(H_2H_3)$ = 9.0)		
	H_5	6.40 (m)		
	H_3	6.33 (m)		
	H_4	6.02 (m)		
 **4**[g]	H_5	7.2[h] ($^3J(H_5H_4)$ = 5.0, $^4J(H_5H_3)$ < 1.0)	C_2	139.42 (dt, $^2J(C_2P_A)$ = 15.6, $^2J(C_2P_M)$ = 3.2)
	H_4	6.47 (dd, $^3J(H_4H_3)$ = 3.2, $^5J(H_4P_A)$ < 1.0)		
	H_3	5.95 (tm, $^4J(H_3P_A)$ = 3.2, $^4J(H_3P_M)$ < 1.0)	C_3	136.10 (d, $^4J(C_4P_A)$ = 4.4)
			C_5	130[c]
			C_4	128.00 (d, $^4J(C_5P_A)$ = 6.7)
 **5**	H_3	6.01 (tm, $^3J(H_3H_2)$ = 11.4, $^3J(H_3H_4)$ = 10.7, $^4J(H_3H_5)$ = 1.8, $^3J(H_3P_M)$ = 2.0)	C_{CO}	168.00 (ddd, $^2J(C_{CO}P_A)$ = 125.4, $^2J(C_{CO}P)$ = 8.2, 5.8)
	H_4	5.46 (dqd, $^3J(H_4H_5)$ = 7.1, $^4J(H_4H_2)$ = 0.5, $^3J(H_4P_M)$ = 2.0)	C_3	138.53 (d, $^2J(C_3P_M)$ = 5.1)
			C_4	124.72 (d, $^2J(C_4P_M)$ = 6.4)
	H_2	3.69 (br dt, $^3J(H_2P_M)$ = $^3J(H_2P_Q)$ = 3.0, $^3J(H_2P_A)$ = 1.0)	C_2	50.03 (dt, $^2J(C_2P_Q)$ = 33.5, $^2J(C_2P_M)$ = 2.5)
	H_5	1.51 (dt, $^4J(H_5P_M)$ = 2.0)	C_5	13.23 (d, $^3J(C_5P_M)$ = 1.5)
 **6**	H_2	4.58 (dd, $^3J(H_2H_3$ = 5.5, $^3J(H_2H_{3'})$ = 10.9)	C_3	48.20 (br s)
	H_3	3.31 (m, $^2J(H_3H_{3'})$ = 13.6, $^3J(H_3H_4)$ = 2.7)	C_2	46.58 (dd, $^2J(C_2P)$ = 10.2, 2.0)
	$H_{3'}$	2.64 (m, $^3J(H_{3'}H_4)$ = 2.0)	C_4	41.99 (dd, $^2J(C_4P)$ = 37.5, 7.2)
	H_5	2.4[i] ($^2J(H_5H_{5'})$ = 2.2)	C_5	20.34 (ddd, $^2J(C_5P)$ = 43.2, 6.0, 2.7)
	H_4	2.2[i] ($^3J(H_4H_{5'})$ = 7.6)		
	$H_{5'}$	1.07 (m)		
 **8**	H_3	7.5[h] ($^3J(H_3H_2)$ = 5.9, $^3J(H_3H_4)$ = 5.3)	C_3	159.22 (q, $^3J(C_3P)$ = 4.2)
	H_2	5.59 (br t, $^4J(H_2P_A)$ = 3.6, $^4J(H_2P_M)$ = 0.8)	C_2	117.22 (dd, $^3J(C_2P_A)$ = 14.6, $^3J(C_2P_M)$ = 2.1)
	H_4	3.1[i] ($^3J(H_4H_5)$ = 7.7)	C_4	42.99 (ddd, $^2J(C_4P_M)$ = 31.9, $^2J(C_4P_Q)$ = 6.9, $^2J(C_4P_A)$ = 2.1)
	$H_{5,5'}$	1.80 (m)		
	H_6	1.52 (dd, $^4J(H_6P_A)$ = 3.5, $^4J(H_6P_M)$ = 1.1)	C_5	35.42 (ddd, $^2J(C_5P_Q)$ = 32.6, $^2J(C_5P_M)$ = 6.9, $^2J(C_5P_A)$ = 2.8)
			C_6	24.55 (dd, $^3J(C_6P_A)$ = 8.2, $^3J(C_6P_M)$ = 1.4)
 **9**[j]	S*Me*	2.40 (d, $^4J(HP_A)$ = 3.8)		
	*H*OCH$_3$	6.21 (s)		
	HOC*H*$_3$	3.92 (s)		
 **10**[k]	S*Me*	2.44 (d, $^4J(HP_A)$ = 3.8)		
	HOC*H*$_2$CH$_3$	4.19 (dq, ^3J(HH) = 7.0, $^4J(HP_M)$ = 3.0)		
	HOCH$_2$C*H*$_3$	1.44 (t)		

[a] All spectra were recorded at room temperature in CD_2Cl_2 solutions unless otherwise stated. [b] Chemical shifts are given in ppm and are relative either to residual ^{1}H resonances in the deuterated solvents (^{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] Masked by the phenyl carbons of the triphos ligand and of the BPh_4^- anion. The chemical shifts were determined from ^{13}C–^{1}H heteronuclear 2D-NMR correlation studies. [d] The ^{13}C{^{1}H} NMR spectrum was recorded in CS_2/C_6D_6, 1:1 (v:v), at room temperature. [e] The ^{1}H NMR spectrum was recorded in THF-d_8 at −50 °C. [f] δ −8.63 (dt, $^2J(HP_Q)$ = 182.2 Hz, $^2J(HP_A)$ = $^2J(HP_M)$ = 7.0 Hz, Ir-*H*). [g] δ −9.15 (dm, second order AA′XX′Y spin system, $|^2J(HP_M) + {}^2J(HP_{M'})|$ = 126.3 Hz, $^2J(HP_A)$ = 13.1 Hz, Ir-*H*). [h] Masked by the aromatic protons of the triphos ligand and of the BPh_4^- anion. [i] Masked by the aliphatic protons of triphos. [j] δ −11.55 (ddd, $^2J(HP_Q)$ = 142.1 Hz, $^2J(HP_M)$ = 12.9 Hz, $^2J(HP_A)$ = 7.5 Hz, Ir-*H*). [k] δ −11.55 (ddd, $^2J(HP_Q)$ = 142.7 Hz, $^2J(HP_M)$ = 12.8 Hz, $^2J(HP_A)$ = 7.6 Hz, Ir-*H*).

coordinated thioether atoms C_6 and C_9 as well as the Ir, P_1, and P_3 atoms lie in one plane (±0.015 Å), which is almost perpendicular to the plane defined by C_7, C_6, C_9 [105(2)°]. The nonplanarity of the butadienethiolate ligand may also be seen in the 68° C_9–C_6–C_7–C_8 torsion angle. The Ir–(C_6–C_9) coordination exhibits a C–C distance [1.55(4) Å] that is among the longest

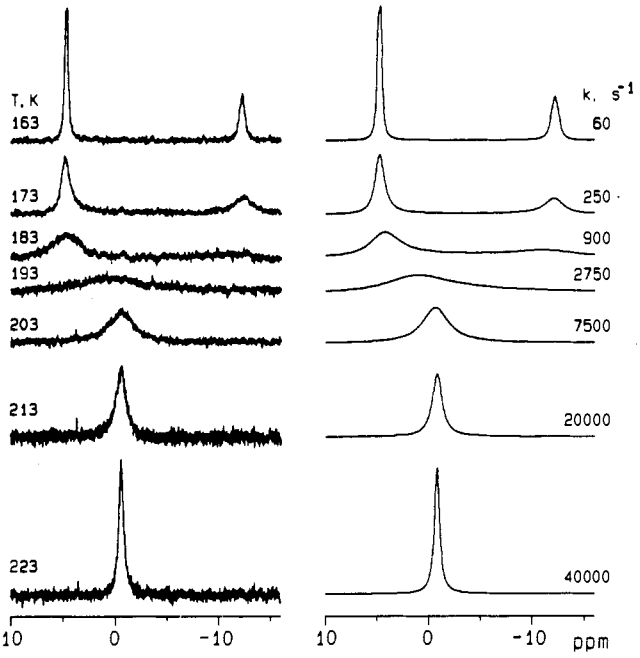


Figure 1. Experimental (left) and computed (right) variable-temperature $^{31}P\{^1H\}$ NMR spectra of **1** in $CD_2Cl_2/CFCl_3$, 2:1 (v:v) (81.01 MHz).

found in metal–η^2-alkene structures, thereby indicating an appreciable amount of metal-to-olefin π-back-bonding (metallacyclopropane structure). However, the coordinated C_6–C_9 separation is shorter than that found in $[CpRu(PPh_2Me)\{\eta^3$-S(Me)C(Me)=CHCH=CH(Me)$\}]BF_4$, which has similarly been prepared by S-methylation of a butadienethiolate precursor.[14a,b]

The crystal structure analysis shows also that the double bond C_7–C_8 [1.38(6) Å] is not coordinated to the metal center, although the electron density in the double bond is probably reduced by the partly positively charged S atom.

Since the ^{31}P, ^1H, and ^{13}C NMR properties of **8** are quite comparable to those of the neutral butadienethiolate precursor **2**, we conclude that the two compounds share the same primary geometry, the only difference being the presence of a methyl group bonded to S in **8** [S_1–C_8 bond distance 1.71(4) Å].

Mechanism for the Formation of 2. (a) Hydride Addition to the Iridathiabenzene Complex. Low-Temperature Experiments. Variable-temperature reaction studies show that the formation of **2** from **1** is actually a two-step process. Indeed, **2** is the thermodynamic product of the hydride addition to **1**, the kinetic product being the Ir(III) hydride [(triphos)IrH(η^2-*C*,*S*-C_4H_4S)] (**3**). Only the latter compound forms, in fact, when **1** in THF is reacted with $LiHBEt_3$ at low temperature. The reaction can conveniently be followed by $^{31}P\{^1H\}$ NMR spectroscopy in THF-d_8; at −50 °C, all **1** converts to **3**, which exhibits an AMQ spin system for the phosphorus nuclei (octahedral structure). As the temperature is increased, **3** selectively transforms into **2**. Complete transformation is achieved by heating the NMR sample at 50 °C for ca. 1 h. Compound **3** is isolable as cream-colored microcrystals (invariably contaminated by 10–30% of the thermodynamic product **2**) by removing the solvent under reduced pressure from the reaction vessel maintained at 0 °C. The presence of a hydride ligand bound to iridium is shown by both the IR spectrum which contains a medium intensity ν(Ir–H) band at 2086 cm^{-1} and the ^1H NMR spectrum which exhibits a doublet of triplets in the hydride region [$J(HP_{trans})$ = 182.2 Hz, $J(HP_{cis})$ = 7.0 Hz]. Four distinct signals for the four methyne hydrogens are observed in the ^1H NMR spectrum with chemical shifts in the expected region of an open η^2-*C*,*S*-C_4H_4S ligand with a localized diene structure.[12c,d,h]

Besides demonstrating the the hydride addition to **1** is mediated by the metal center (thus ruling out a direct nucleophilic addition to C_5), the **3** → **2** thermal rearrangement most importantly accounts for the regiospecificity of the hydride addition to the iridathiabenzene ring. Such a reaction, in fact, may be seen as occurring via a simple reductive elimination step of *cis* hydride and vinyl ligands in intermediate **3**.

(b) Alternative Synthesis. Compound **2** can straightforwardly be prepared by treatment of a THF suspension of the dihydride(ethyl) complex [(triphos)Ir$(H)_2(C_2H_5)$][22] with an excess of thiophene at reflux temperature. Interestingly, the formation of **2** is accompanied by that of a minor species, namely the octahedral dihydride(2-thienyl) complex [(triphos)Ir$(H)_2$(2-C_4H_3S)] (**4**), which has fully been characterized by NMR and IR spectroscopies. Compounds **2** and **4** invariably form in a 6:1 ratio regardless of either the initial concentration of the starting dihydride(ethyl) complex or the reaction time. Low-temperature-reaction studies are precluded by the necessity of using a relatively high temperature (ca. 70 °C) to promote the reductive elimination of ethane (detected by ^1H NMR and GC) from the dihydride(ethyl) complex. Although **2** and **4** can be easily separated due to their highly different solubility in THF/*n*-hexane mixtures, analytically pure samples of **4** are better obtained by an alternative synthetic procedure. This involves treatment of the known dihydride(chloride) complex [(triphos)Ir$(H)_2Cl$][24] in THF with 2-LiC_4H_3S.

The observation that **4** does not convert to **2** in THF up to 100 °C even in the presence of an excess of thiophene provides two valuable pieces of mechanistic information. First, the thienyl complex **4** is not a kinetic intermediate for the C–S cleavage of thiophene at iridium, as conversely observed by Jones and coworkers for the intramolecular thermal rearrangement of [Cp*Rh(PMe_3)(2-thienyl)H] to [Cp*Rh(PMe_3)(η^2-*C*,*S*-C_4H_4S)].[12d] Second, the cleavage of thiophene does occur at a 16-electron fragment, in the case at hand [(triphos)IrH], which is generated in situ by the reductive elimination of ethane from the dihydride(ethyl) complex.[16]

The chemistry of the 16-electron fragment [(triphos)IrH] is extensively investigated in our laboratory. It has been found that it reacts with ethylene to give, as kinetic product, the dihydride(vinyl) complex [(triphos)Ir$(H)_2(C_2H_3)$],[35] which then thermally rearranges to the thermodynamically more stable η^2-C_2H_4 derivative [(triphos)Ir(H)(C_2H_4)].[22] Accordingly, we suggest that the thienyl complex **4** may form via a direct C–H bond activation path of thiophene at iridium without passing through an η^2-thiophene intermediate. In contrast, the latter species may be important in the formation of an allyl sulfide intermediate, obtained by hydride migration from iridium to η^2-thiophene, which then undergoes C–S bond cleavage to yield the butadienethiolate complex **2**. An allyl sulfide complex has already been suggested by Angelici to be a possible intermediate in the reaction between hydride and the η^5-2,5-dimethylthiophene complex [CpRu(η^5-2,5-dimethylthiophene)]PF_6 yielding the butadienethiolate derivative CpRu(η^5-SC(Me)=CHCH=CH(Me)).[14a,b] However, as suggested by Jones, it is also possible that thiophene first coordinates to the soft iridium(I) center of the [(triphos)IrH] fragment via its sulfur atom and then one of the two α-carbons undergoes a sulfur-to-metal migration to form the thermally unstable complex **3** which then rearranges to **2**.[12d]

Reactions of the Butadienethiolate Complex 2 with Proton Sources. Complex **2** is quite robust in both the solid state and solution. Heating **2** in refluxing THF causes little or no decomposition even in the presence of strong ligands such as CO and PEt_3. However, **2** undergoes a number of interesting hydrogenation reactions with various protic acids.

Reaction with H^+/CO. The first reaction was attempted on **2** was the one with a protic acid in order to mimick the sequential

(35) Bianchini, C.; Meli, A., manuscript in preparation.

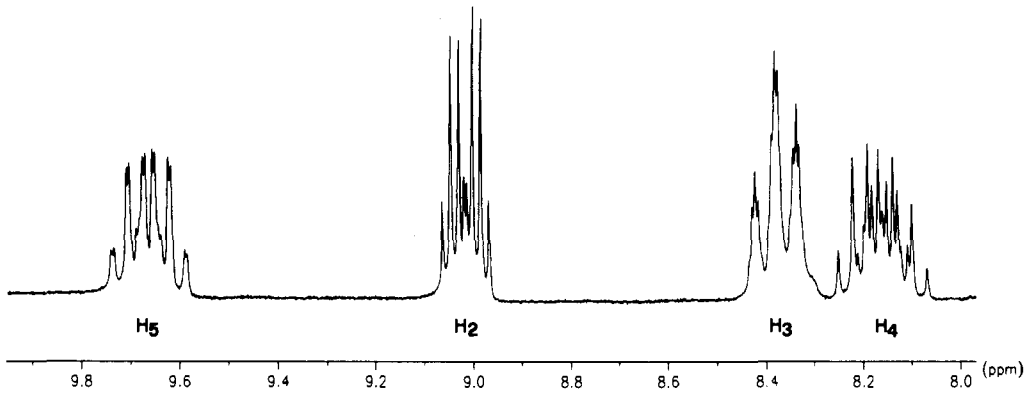


Figure 2. ^1H NMR spectrum of the methyne protons of thiophene in **1** in CD_2Cl_2 at 20 °C (200.13 MHz).

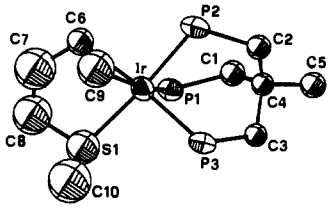


Figure 3. ORTEP drawing of the complex cation $[(triphos)Ir\{\eta^3\text{-}S(Me)CH{=}CHCH{=}CH_2\}]^+$ in **8**. All of the hydrogen atoms and phenyl rings of triphos are omitted for clarity.

Table III. Selected Bond Distances (Å) and Angles (deg) for **8**

Ir–P1	2.362(7)	C6–Ir–P1	115.4(7)
Ir–P2	2.323(7)	C6–Ir–P2	153.2(7)
Ir–P3	2.283(7)	C6–Ir–P3	91.2(7)
Ir–S1	2.36(1)	C9–Ir–P1	157.4(9)
Ir–C6	2.19(3)	C9–Ir–P2	111.2(9)
Ir–C9	2.12(3)	C9–Ir–P3	92(1)
S1–C8	1.71(4)	S1–Ir–P1	94.9(3)
S1–C10	1.71(4)	S1–Ir–P2	95.7(3)
P1–C1	1.87(3)	S1–Ir–P3	174.3(3)
P2–C2	1.88(2)	C6–Ir–C9	42(1)
P3–C3	1.89(3)	C6–Ir–S1	83.5(8)
C1–C4	1.55(3)	C9–Ir–S1	83.1(9)
C2–C4	1.56(3)	Ir–S1–C10	111(1)
C3–C4	1.53(3)	Ir–S1–C8	103(1)
C4–C5	1.51(3)	C8–S1–C10	102(2)
C6–C7	1.53(5)		
C6–C9	1.55(4)		
C7–C8	1.38(6)		

addition of H^-/H^+ to cleaved thiophene, a reaction sequence that is believed to occur in the first steps of the heterogeneous HDS process.[9,36]

To a THF solution of **2** was added a stoichiometric amount of $HBF_4{\cdot}OEt_2$. Immediately the yellow solution turned red. Workup as usual (addition of either ethanol or *n*-hexane, or removal of the solvent in vacuo) invariably gave an amorphous product, which was revealed to contain innumerable metal complexes by NMR spectroscopy. We decided therefore to study the reaction by variable-temperature NMR spectroscopy in THF-d_8. Interestingly, protonation at low temperature (–40 °C) shows that only one species forms, which exhibits a well-resolved ^{31}P NMR AMQ spin system (see Experimental Section). Although of poor quality due to the presence of diethyl ether, the ^1H NMR spectrum clearly shows that the red product does not contain hydride ligands bound to iridium. Increasing the temperature causes slow decomposition of the initial product. At room temperature, complete conversion to several metal species occurs within 30 min.

Intrigued by the possibility of chemically trapping the first protonation product, we carried out the reaction of **2** with HBF_4 in the presence of carbon monoxide (1 atm) (recall that CO does not react with **2**). As a result, a pale yellow solution was obtained after 10 min of stirring at room temperature from which off-white crystals of $[triphos)Ir(CO)\{\eta^4\text{-}S{=}CHCH{=}CH(Me)\}]BF_4$ (**5**) precipitated in good yield.

(36) Choi, M.-C.; Daniels, L. M.; Angelici, R. J. *Inorg. Chem.* **1991**, *30*, 3647 and references therein.

Table IV. Summary of Crystal Data for **8**

formula	$C_{71}H_{70}BIrO_{0.5}P_3S$
formula wt, g mol^{-1}	1259.25
cryst dimensions, mm	0.30 × 0.20 × 0.08
cryst system	monoclinic
space group	$P2_1/n$ (No. 14)
a, Å	32.431(4)
b, Å	18.631(3)
c, Å	9.957(6)
V, Å^3	6016.10
Z	4
ρ_{calc}, g cm^{-3}	1.39
μ(Mo Kα), cm^{-1}	23.62
radiation	graphite-monochromated Mo Kα, λ = 0.71069 Å
scan type	ω
2θ range, deg	5–45
scan width, deg	0.8 + 0.35(tan θ)
scan speed, deg min^{-1}	8.24
total no. of data	8688
no. of unique data, $I > 3\sigma(I)$	3287
no. of parameters	226
R	0.081
R_w	0.083

Compound **5** is stable in both the solid state and deoxygenated solutions in which it behaves as a 1:1 electrolyte. The IR spectrum contains a strong absorption at 2042 cm^{-1}, which is assigned to a terminal carbonyl ligand, as confirmed also by a resonance at 168.0 ppm in the $^{13}C\{^1H\}$ NMR spectrum. Like the neutral precursor **2**, compound **5** is stereochemically rigid on the NMR time scale, the $^{31}P\{^1H\}$ NMR spectrum consisting of a temperature-invariant AMQ spin system. The site of attack of the added proton is clearly shown by ^1H and ^{13}C-DEPT spectra, and particularly by 2D-NMR spectroscopy (H,H-COSY and H,C-HETCOR, Figure 4) and heteronuclear $^1H\{^{31}P\}$ selective decoupling experiments. Surprisingly, a methyl group [δ 1.51, $^4J(HP_M)$ = 2.0 Hz] is now bonded to C_4, thus indicating that the entering hydrogen atom has selectively been delivered to the terminal carbon atom (C_5) of the butadienethiolate ligand in **2**. However, the most surprising structural feature of the C_4H_6S ring in **5** is provided by analysis of the J(CP) and J(HP) values. Indeed, the strongest couplings are those between the C_2–H_2 methyne group, i.e. the one proximal to sulfur, and the P_Q nucleus [$^2J(C_2P_Q)$ = 33.5 Hz, $^3J(H_2P_Q)$ = 3.0 Hz]. In contrast, both the C_3–H_3 and C_4–H_4 groups are weakly coupled to the P_M only [$^2J(C_3P_M)$ = 5.1 Hz, $^3J(H_3P_M)$ = 2.0 Hz, $^2J(C_4P_M)$ = 6.4 Hz, $^3J(H_4P_M)$ = 2.0 Hz]. Finally, H_3 and H_4 are rather strongly coupled to each other (10.7 Hz) and weakly coupled to H_2 [$^4J(H_4H_2)$ = 0.5 Hz].

From a perusal of the J(HH), J(HP), and J(CP) coupling network, it is reasonable to conclude that the butadienethiolate

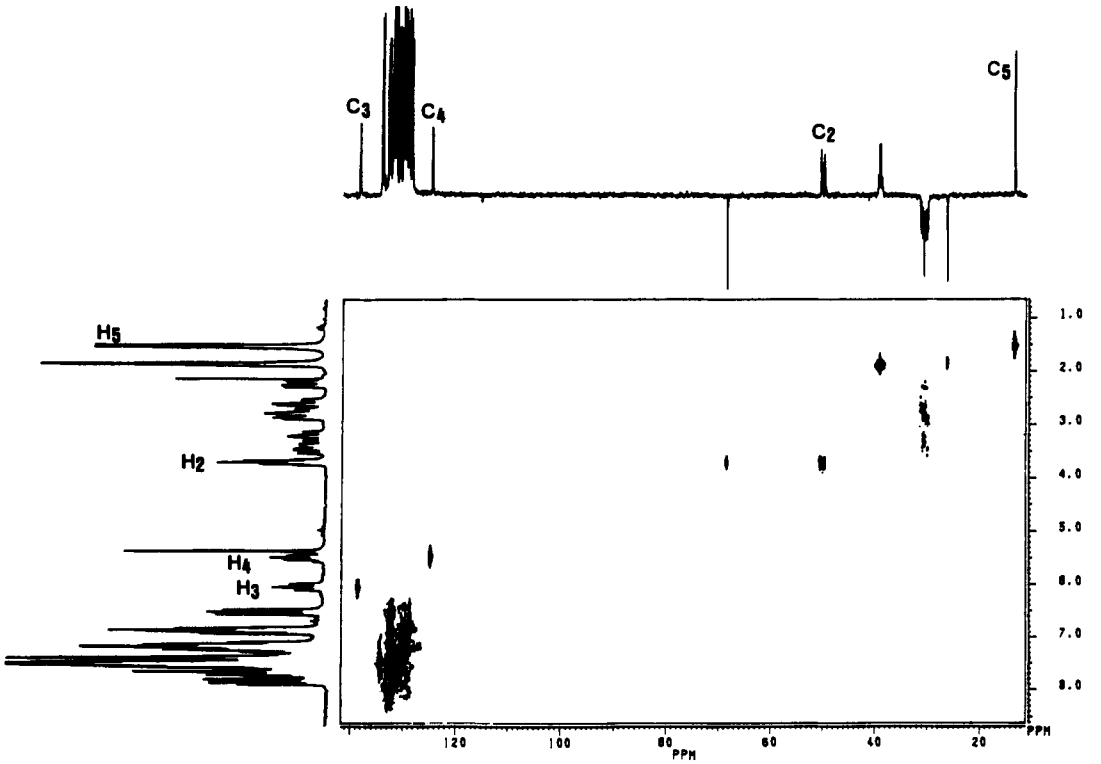


Figure 4. $^{13}C-^{1}H$ heteronuclear 2D-NMR correlation study of **5** in CD_2Cl_2 at 20 °C. The horizontal trace shows a DEPT experiment for separation of CH_2 (negative) from CH and CH_3 carbon atoms (positive).

ligand in **2** has transformed into thiocrotonaldehyde (CH_3)-CH=CH(CHS). The latter ligand uses the C–S bond to strongly bind the metal center *trans* to P_Q (due to the short bite provided by a dihapto C–S bond, this may be seen as occupying a single coordination site). The octahedral structure of the complex is then completed by a weaker interaction with the C_4 and C_3 carbons of the alkene moiety *trans* to P_M.

The spectroscopic observation (NMR) that no intermediate species precedes the formation of **5** might lead to the conclusion that the kinetic product of the protonation of **2** is an unstable thiocrotonaldehyde complex which is then stabilized by CO coordination. We have no evidence for contrasting such a hypothesis. However, in light of other experiments (see forthcoming pages) as well as the result of the chemoselective methylation reaction of **2**, it is apparent that the sulfur atom of the butadienethiolate ligand in **2** is an excellent nucleophile. Accordingly, the protonation of **2** might take place initially at the sulfur atom, to give a butadiene-1-thiol ligand, and only at a later stage, i.e. after CO coordination, the proton would be transferred to the terminal carbon atom (C_5) of the bound alkene moiety through the conjugated diene system.

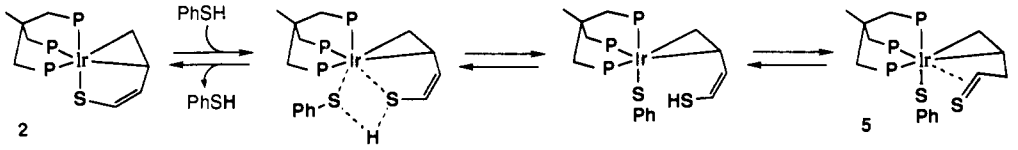
Reaction with PhSH. It has been suggested that an important step in the heterogeneous HDS process involves proton transfer from M–SH units present on the catalyst surface to M–thiophene moieties.[9] With this in mind, we decided to explore the reaction of **2** in THF with an organic thiol such as thiophenol. Indeed, a fast reaction occurs at room temperature, which quantitatively converts **2** to [(triphos)Ir(SPh)(η^4-S=CHCH$_2$CH=CH$_2$)] (**6**).

Compound **6** is isolated as pale yellow crystals which are stable in the solid state, but slowly transform into **2** and free PhSH in solution. The process is reversible, i.e. addition of an excess of PhSH quantitatively restores **6**. The $^{31}P\{^1H\}$ NMR spectrum consists of a temperature-invariant AMQ spin system. Unlike the reaction of **2** with H^+/CO, the proton of PhSH appears to be selectively delivered to the C_3 carbon atom of the butadienethiolate ligand, which is thus converted to an allylthioaldehyde molecule. This uses the alkene moiety (C_5–C_4) and the C–S bond to coordinate the metal center in a tetrahapto fashion, as is unambiguously shown by NMR spectroscopy. The ^1H NMR spectrum exhibits six distinct signals for the six hydrogen atoms of the C_4H_6S moiety, four of which (H_5, $H_{5'}$; H_3, $H_{3'}$) constitute two diastereotopic pairs. The presence of two methylene groups, $C_3(H_3H_{3'})$ and $C_5(H_5H_{5'})$, is substantiated by ^{13}C-NMR DEPT experiments.

From an inspection of the positions of the carbon resonances in the $^{13}C\{^1H\}$ NMR spectrum as well as their coupling constants to the P nuclei, one can readily infer that unlike the thiocrotonaldehyde complex **5**, the alkene moiety in **6** is strongly bound to the metal center [C_5 20.34 ppm, $^2J(C_5P)$ = 43.2, 6.0, 2.7 Hz; C_4 41.99 ppm, $^2J(C_4P)$ = 37.5, 7.2 Hz]. In contrast, a weaker but effective interaction of the C–S bond with the metal center is suggested by a rather small coupling of C_2 to the phosphorus nuclei [$^2J(C_2P)$ = 10.2, 2.0 Hz]. In accord with the proposed structure of **6**, C_3, H_3, $H_{3'}$, and H_2 do not show appreciable coupling to the phosphorus atoms, whereas $H_{5'}$ is coupled to phosphorus ($^1H\{^{31}P\}$ experiment). However, due to the complicated pattern of the $H_{5'}$ resonance, no reliable J(HP) value can be given. In a similar way, both H_5 and H_4 are expected to couple to the phosphorus nuclei even though this cannot be proved because both resonances are masked by those of the aliphatic hydrogens of the ligand backbone (a 2D-COSY experiment simply provides their chemical shift values). Finally, the presence of a thiophenolate ligand bound to iridium is shown by IR spectroscopy (reinforced phenyl vibration at 1580 cm^{-1}) and molar conductivity measurements (the compound is a nonelectrolyte).

From a mechanistic viewpoint, the formation of **6** may initially proceed via heterolytic splitting of the S–H bond of PhSH. As a result, protonation of **2** at the sulfur atom occurs to give a butadiene-1-thiol ligand, followed by proton transfer from sulfur to the C_3 carbon atom of the proximal uncomplexed alkene moiety. The latter step may formally be seen as an enol–keto tautomerization assisted by the metal center. In the solid state and in solution in the presence of an excess of PhSH as well, the keto form is more stable than the enol form. In contrast, a slow reisomerization to the enol form may take place in solution, in which case PhSH can be eliminated via an intramolecular acid/base interaction (Scheme III). Reaction of **6** with PhSD shows

Scheme III



that deuterium is regiospecifically but not stereospecifically incorporated at C_3, which is in agreement with the proposed mechanism.

An alternative pathway could involve coordination of the thiol to iridium, followed by direct intramolecular proton migration to C_3. This mechanism, however, is unlikely, as it would involve a 20-e intermediate unless either phosphorus donor or the thiolate sulfur is displaced by the weaker thiol ligand.

Reaction with HCl. Stirring a THF solution of **2** with a 5-fold excess of gaseous HCl at room temperature results in the complete destruction of the original complex framework. All iridium is recovered as the known Ir(III) trichloride [(triphos)$IrCl_3$], whereas four different products are obtained from the butadienethiolate ligand. The two major products, H_2S and buta-1,3-diene (ca. 70% yield based on the starting amount of **2**), are evidently generated by a C–S cleavage reaction as occurs in the HDS process. The other two products are the unsaturated thiols 3-butene-1-thiol and 1-butene-1-thiol in a ca. 4:1 ratio (GC/MS).

The reaction between **2** and HCl is too fast so as to preclude any mechanistic interpretation based on spectroscopic measurements. Nevertheless, the reaction is per se remarkable as it shows that the sequential addition of H^-/H^+ to ring-opened thiophene may lead to highly hydrogenated species.

Reaction of the Thioether Complex 8 with HCl. Unlike the butadienethiolate precursor **2**, the thioether complex **8** does not react with H^+ from either HBF_4 or $HOSO_3CF_3$. This is not completely unexpected in light of the positive charge of the complex as well as the reduced nucleophilicity of the sulfur atom. In contrast, **8** rapidly reacts with a 5-fold excess of gaseous HCl converting to the trichloride [(triphos)$IrCl_3$] and evolving the unsaturated thioethers CH_2=$CHCH_2CH_2SMe$ and CH_3CH_2-CH=CHSMe in a 1:2 ratio (GC/MS).

Homogeneous metal-assisted degradations of thiophene to unsaturated thiols or thioethers of the types obtained by us are unprecedented. The only comparable reaction has recently been reported by Angelici, who was capable of removing the buta-1,3-dienyl methyl thioether CH_2=CHCH=CHSMe from [(CpRu(PPh_2Me)(η^3-S(Me)CH=CHCH=CH_2)]$^+$ by addition of 2 equiv of PPh_2Me.[14b]

Reaction of 8 with THF·BH_3. An electrophilic reagent that brings about the desulfurization of the buta-1,3-dienyl methyl thioether ligand in **8** is THF·BH_3. Unexpectedly (the reaction between **8** and borane was just an attempt to hydroborate the uncomplexed double bond in the molecule), treatment of **8** in THF with a 4-fold excess of THF·BH_3, followed by MeOH or EtOH addition, produces off-white crystals of [(triphos)IrH(SMe)(ROH)]BPh_4 (R = Me, **9**; Et, **10**) and evolves buta-1,3-diene. A reaction between **8** and borane occurs also in the absence of alcohol. In this case, however, the product is very unstable and rapidly decomposes to give unidentified metal species, buta-1,3-diene, and traces of MeSH. The instability of the primarily generated product is shown by the fact that rather low yields of **9** and **10** (ca. 50%) are obtained even by addition of alcohol. In contrast, both compounds, once isolated, are quite stable in both the solid state and solution.

Compounds **9** and **10** are stereochemically rigid in solution on the NMR time scale, the $^{31}P\{^1H\}$ NMR spectra consisting of temperature-invariant (−80/+30 °C) AMQ spin systems. The octahedral geometry around iridium in both complexes is completed by a terminal hydride (δ −11.55, ddd structure), a methyl sulfide ligand [$^2J(HP_A)$ = 3.8 Hz], and an alcohol molecule. Unambiguous evidence of the presence of an alcohol molecule bonded to iridium is provided by the ^1H NMR spectra which show significant shifts of the ROH hydrogen resonances with respect to those of the free alcohols in the same solvent. Also, coupling to one phosphorus nucleus is found for the methylene hydrogens of ethanol [$^3J(HP_M)$ = 3.0 Hz].

Compound **9** (**10**) in CH_2Cl_2 converts to **10** (**9**) by addition of an excess of EtOH (MeOH). It is therefore reasonable to have found that by treatment of both compounds in CH_2Cl_2 with a slight excess of either MeOD or EtOD the coordinated alcohol molecule is displaced by the corresponding deuterated alcohol. In contrast, it is surprising that no isotope H/D exchange is observed between the terminal hydride ligand and the *cis* MeOD or EtOD ligands in [(triphos)IrH(SMe)(ROD)]$^+$. This finding is extremely important for the mechanistic interpretation of the following experiment. When the reaction of **8** with borane in dry THF is followed by addition of either MeOD or EtOD, still the complexes contain Ir–H bonds, while no incorporation of deuterium into buta-1,3-diene is observed. Accordingly, one may conclude that (i) the role of the alcohol is just that of stabilizing the (triphos)IrH(SMe)$^+$ fragment and (ii) borane is a reagent for the cleavage of the C–S bond. It remains to ascertain the mechanism of the interaction with borane which, as an electrophilic reagent, might attack the residual lone pair of the sulfur atom.[37] In this case, hydrogen transfer from borane to the close C_2 carbon atom would cleave the C–S bond and give buta-1,3-diene. However, since an excess of THF·BH_3 is necessary to accomplish the reaction, one cannot exclude the occurrence of a multistep reaction.

Conclusions

The present work sheds some light on an area of much current interest in chemistry, namely the homogeneous metal activation of thiophenic compounds.

With the combination of a tripodal polyphosphine ligand such as triphos and of a kinetically inert third-row transition metal such as iridium, we have been able to synthesize and characterize an unforeseen variety of ligands and free molecules derived from the opening, fragmentation, or hydrogenation of thiophene.

Surveying the results presented in this paper, one may draw several conclusions, some of which certainly increase the molecular level understanding of thiophene HDS. In particular, the following results deserve comment.

(i) Electron-rich metal systems favor ring-opening of thiophene, consistent with previous literature data.[12]

(ii) The hydride addition to metallathiabenzene complexes can occur via metal–hydride intermediates, a reaction path that has never been proved before.

(iii) The sulfur atom of the open C_4H_5S ring is a nucleophilic center, as shown by the reaction with MeI. It is conceivable that this sulfur atom can also mediate hydrogenation paths involving subsequent H^+ addition.

(iv) The C–H bond activation thienyl products may not be in general kinetically significant for the opening of thiophene. Accordingly, metal systems that favor C–H bond cleavage may not always be appropriate for thiophene opening.

(v) Thiol groups can hydrogenate thiophene metallarings via intramolecular proton transfers, a reaction path that has been suggested to occur during the heterogeneous HDS.[9]

(37) Braun, R. A.; Brown, D. C.; Adams, R. M. *J. Am. Chem. Soc.* **1971**, *93*, 2823.

(vi) Strong protic acids or hydrogen-releasing electrophiles may replace H_2 in the fragmentation of thiophene to H_2S and buta-1,3-diene.

(vii) The observation that the iridathiabenzene complex **1** is stable under H_2 atmosphere even in refluxing THF, whereas it readily reacts in a stepwise manner with H^+/H^-, suggests that the heterolytic splitting of H_2 on the HDS catalyst may be an important step of the reaction. In this respect, it is worth mentioning a fascinating work recently reported by Curtis and co-workers who have demonstrated that a discrete Co–Mo cluster containing sulfido bridges functions as a desulfurization catalyst for thiophene under H_2.[13b] Although these investigators did not mention the way of activation of H_2, it may be the case that dihydrogen is heterolytically split to give S–H and M–H groups, as has been proved to occur in the reversible addition of H_2 on the bis(μ-sulfido) complex [(triphos)Rh(μ-S)$_2$Rh(triphos)](BPh$_4$)$_2$.[38]

Acknowledgment. Thanks are due to Mr. Dante Masi for collecting X-ray data.

Supplementary Material Available: Final positional parameters and refined anisotropic and isotropic temperature factors for all non-hydrogen atoms (Table S1) and final positional parameters for hydrogen atoms for **8** (Table S2) (4 pages); a listing of observed and calculated structure factors for **8** (19 pages). Ordering information is given on any current masthead page.

(38) Bianchini, C.; Meli, A. *Inorg. Chem.* **1987**, *26*, 4268.