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C–H bond activation of thiophenes at iridium: a lower energy process than C–S bond scission

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Abstract

The 16-electron fragment [(triphos)IrH], generated in situ by thermolysis of (triphos)Ir(H)$_2$(C$_2$H$_5$) in THF, reacts with thiophene (**T**) or benzo[*b*]thiophene (**BT**) to give, in the temperature range from 67 to 100 °C, mixtures of C–H and C–S insertion products as a result of parallel reactions [triphos = MeC(CH$_2$PPh$_2$)$_3$]. Above 100 °C, the (thienyl)dihydride complexes convert to the thermodynamically more stable C–S insertion products (butadienethiolate and 2-vinylthiophenolate complexes) through an intramolecular mechanism which does not involve **T** or **BT** dissociation. A comparison is made to analogous reactions with dibenzothiophene.

Keywords: Iridium; Thiophene; C–H activation; Hydrodesulfurization; Phosphine; Thiolate

1. Introduction

The study of the coordination and reactivity of thiophenes with soluble metal complexes constitutes a modeling approach for the elucidation of the HDS mechanism over heterogeneous catalysts [1]. Several bonding modes of model substrates such as thiophene (**T**), benzo[*b*]thiophene (**BT**) and dibenzothiophene (**DBT**), as well as reactions leading to C–S bond cleavage, hydrogenation and desulfurization, have been described in detail [1–10].

With a few exceptions [2,3,5], C–S bond scission occurs when the activating metal complex is a highly energetic 16-electron species of the types shown in sketches I–IV [2,7,8,11–13]. For steric reasons, these metal fragments cannot exist in a square-planar geometry and thus are excellent candidates for the oxidative cleavage of chemical bonds owing to their capability for lowering the energy barrier to insertion [14,15].

Since thiophenes possess both C–S and C–H bonds which can be cleaved upon dπ (metal) $\rightarrow$ σ^* (ligand) electron-transfer [1b], the reactions with electron-rich metal fragments may produce either metallathiacycles or thienyl(hydride) complexes. In a number of cases, both types of insertion take place in parallel reaction paths [2,7,8,11]. When this occurs, it is generally observed that C–H bond cleavage is kinetically competitive with C–S bond cleavage, but the latter is thermodynamically preferred [2,11].

The conversion of thienyl(hydride) metal complexes to metallathiacycles may proceed by either an intramolecular or an intermolecular reaction coordinate. An intramolecular rearrangement, without dissociation of the thiophene, has been observed by Jones et al. for the activation of **T** on the fragment [(C$_5$Me$_5$)Rh(PMe$_3$)] [11a]. In contrast, the occurrence of a dissociative mechanism has been demonstrated for the conversion of a mixture of the dibenzothienyl isomers (triphos)-Ir(H)$_2$(DBTyl) [DBtyl = 4-, 3- and 2-C$_{12}$H$_7$S] to the C–S insertion product (triphos)IrH(η^2-*C,S*-DBT) [triphos = MeC(CH$_2$PPh$_2$)$_3$] [12] (Scheme 1).

No mechanistic information is currently available for the analogous rearrangements of benzo[*b*]thienyl hydride complexes to benzothiabenzene products.

In the present paper, we describe the interaction of the unsaturated fragment [(triphos)IrH] with **T** and **BT** under different reaction conditions. From this study, it is also concluded that the mechanism of the thienyl(hydride) $\rightarrow$ metallathiacycle rearrangement is governed

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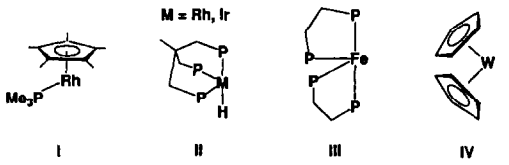


by the nature of the thiophenic molecule rather than by the nature of the metal fragment.

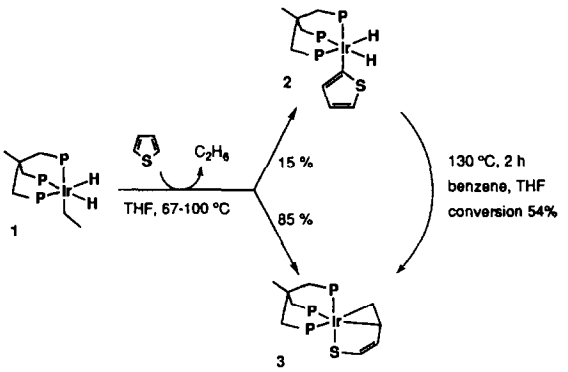
2. Results and discussion

It has recently been reported that the fragment [(triphos)IrH], generated in situ by thermolysis of (triphos)Ir(H)$_2$(C$_2$H$_5$) (**1**) in THF at 67 °C, reacts with **T** to give a mixture of the 2-thienyl complex (triphos)Ir(H)$_2$(2-Tyl) (**2**) and the butadienethiolate complex (triphos)Ir(η^3-SCH = CH–CH = CH$_2$) (**3**) in a ratio of 15 to 85 (Scheme 2) [2]. Since this product composition does not change with time up to 100 °C, it was concluded that, in the temperature range under investigation, the thienyl complex **2** was not a kinetic intermediate for the C–S cleavage of **T** at iridium.

We have now found that the conversion of **2** to **3** does occur in solution as a thermal step above 100 °C. At 130 °C, in either THF or benzene, a pure sample of **2**, independently prepared by treatment of (triphos)Ir(H)$_2$Cl with 2-thienyllithiun [2], converts to **3** (54% conversion in 2 h) (Scheme 2).

No formation of (triphos)Ir(H)$_2$(C$_6$H$_5$) (**4**) is observed even after prolonged heating (24 h) in benzene. On the other hand, thermolysis of **1** in benzene at 100 °C in the presence of a 5-fold excess of **T** exclusively gives **4**. These results unambiguously indicate that the rearrangement of **2** to **3** proceeds via an intramolecular mechanism (vide infra). In fact, should **T** dissociate from **2**, benzene (of which there is a very large excess) would trap the reactive fragment [(triphos)IrH] through the formation of the stable (phenyl)dihydride **4** [14]. Indeed, the selective formation of **4** does occur when the thermolysis of the dibenzothienyl complex (triphos)Ir(H)$_2$(4-DBTyl) is carried out in benzene rather than in THF [12].

The interaction of [(triphos)IrH] with **BT** proceeds in a manner which closely resembles that with **T**. In fact, thermolysis of **1** in refluxing THF in the presence of an excess of **BT** for 24 h gives a 13:87 mixture of the (benzothienyl)dihydride complex (triphos)Ir(H)$_2$(2-BTyl) (**5**) [2-BTyl = 2-benzo[*b*]thienyl] and the 2-vinylthiophenolate (triphos)Ir(η^3-S(C$_6$H$_4$)CH = CH$_2$) (**6**) [3]. Further heating up to 100 °C does not change this product distribution (Scheme 3).

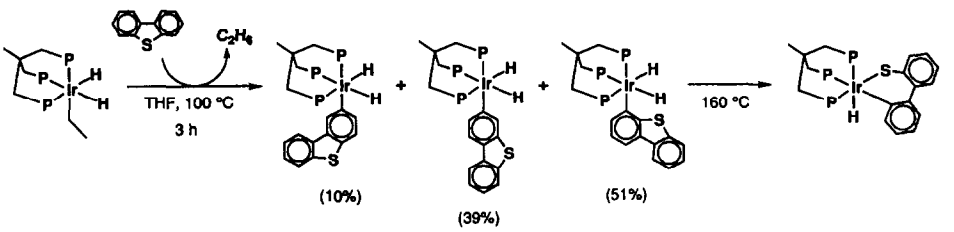


Scheme 2.

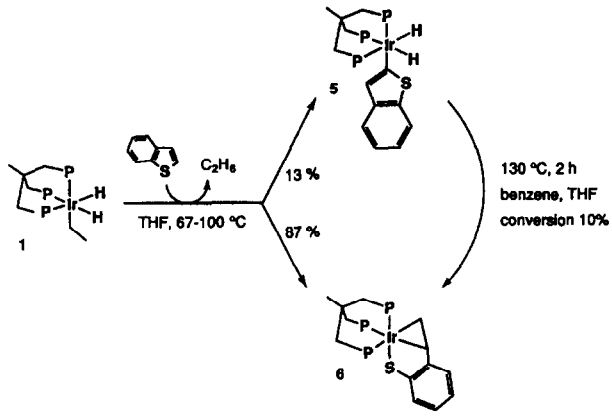
A parallel experiment carried out in a sealed NMR tube has provided the following pieces of information. Two products are initially formed at the expense of **1**: the hydride (triphos)IrH(η^2-*C,S*-C$_8$H$_6$S) (**7**) [3] and, in smaller amounts, the (benzothienyl)dihydride **5**. As the thermolysis of **1** proceeds, at a constant temperature of 67 °C, the concentration of **5** slowly increases until the starting complex has been totally consumed (5 h). After **1** has been consumed, the amount of **5** does not change with time. In the meantime, the concentration of the (metallacycle)hydride **7**, after a rapid increase within the first hour, slowly decreases due to the isomerization of **7** to the 2-vinylthiophenolate complex **6** (Fig. 1).

From an examination of Fig. 1, one may readily infer that (i) the C–H (**5**) and C–S insertion products (**7** and **6**) form in parallel reactions, (ii) the iridathiacycle **7** is the kinetic product of the C–S scission reaction at the [(triphos)IrH] fragment, and (iii) the activation energy for the C–S bond scission reaction (formation of **7**) is lower than that for the C–H bond scission (formation of **5**).

The mechanism of the isomerization of **7** to **6** has recently been studied through an alternative synthesis of **7**. This synthesis involved hydride addition to the iridathiabenzene complex [(triphos)Ir(η^2-*C,S*-SC$_8$H$_6$)]BPh$_4$



Scheme 1.



Scheme 3.

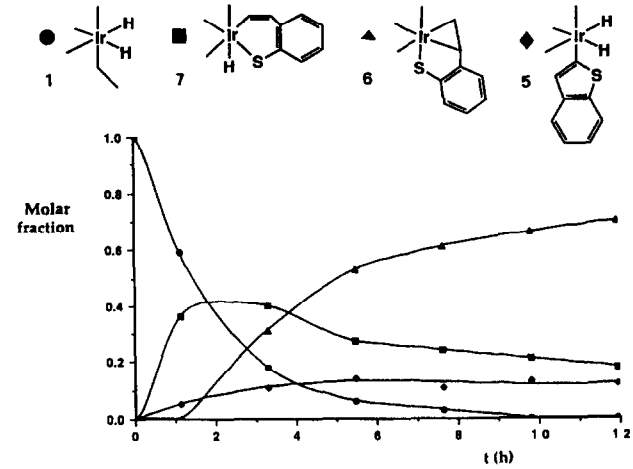


Fig. 1. Distribution of species in the course of the reaction between (triphos)Ir(H)$_2$(C$_2$H$_5$) and benzo[*b*]thiophene at 67 °C in THF-d_8.

(**8**) to give **7** [3] (Scheme 4). The thermal isomerization of **7** to **6** proceeds intramolecularly via the regioselective coupling of the terminal hydride to the α-carbon of the thiacycle.

Above 100 °C, the (BTyl)dihydride **5** in either THF or benzene transforms into the C–S insertion product **6** via the hydride complex **7**. Like the analogous reaction of the (Tyl)dihydride **2**, this rearrangement must proceed through an intramolecular mechanism, as no (phenyl)dihydride complex **4** is observed in the course of the thermolysis reaction of **5** in benzene (Scheme 3).

3. Conclusions

The fragment [(triphos)IrH] reacts with **T** or **BT** at temperatures lower than 100 °C by preferential insertion into the C–S bond, with a detectable amount of C–H bond cleavage products formed in a parallel reaction. Above 100 °C, the C–H insertion products convert to the C–S insertion products through a mechanism that does not involve **T** or **BT** dissociation.

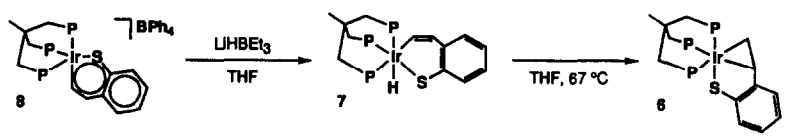
The present results are consistent with a previous report by Jones on the activation of **T** using the system [(C$_5$Me$_5$)Rh(PMe$_3$)] [11a], but markedly contrast with a recent report from our laboratories on the conversion of (triphos)Ir(H)$_2$(4-DBTyl) to (triphos)IrH(η^2-*C,S*-DBT) [12].

As suggested by Jones, η^2-complexation of rhodium to a **T** C–C double bond can lead to the production of the C–H activation products. There is no reason to exclude a mechanism of this type to explain the formation of the present Tyl and BTyl iridium complexes upon interaction of [(triphos)IrH] with the corresponding thiophene. In solution, both thienyl complexes may thus be in equilibrium with η^2-*C,C*- species up to 100 °C. Above this temperature, a change in the bonding mode to either **T** or **BT** from η^2-*C,C* to η^1-*S* probably occurs to give an *S*-bound intermediate, which is believed to be the immediate precursor to C–S bond cleavage. Since this process is intramolecular in character, one may envisage a slippage of the metal center from the double bond to the sulfur atom. Such a process is evidently unattainable by the **DBT** C–H insertion products, which, upon C–H reductive coupling, cannot form a transient η^2-*C,C*-**DBT** species. The reductive elimination step thus liberates **DBT**, which can recombine with the fragment [(triphos)IrH] to give first an η^1-*S*-**DBT**, and eventually a C–S cleavage product, provided there is an input of energy sufficient to overcome the barrier to insertion.

4. Experimental section

4.1. 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 benzo[*b*]thiophene (BT, Aldrich) was sublimed prior to use. *n*-Butyllithium (1.6 M solution in hexanes) was



Scheme 4.

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(H)$_2$(C$_2$H$_5$) [16], (triphos)Ir(H)$_2$Cl [16], and (triphos)Ir(H)$_2$(2-Tyl) [2]. 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. ^{1}H NMR spectra were obtained on a Bruker ACP 200 (200.13 MHz) spectrometer. ^{1}H NMR shifts are recorded relative to residual ^{1}H resonance in the deuterated solvent. ^{31}P{^{1}H} NMR spectra were recorded on a Bruker ACP 200 spectrometer operating at 81.01 MHz. Chemical shifts are relative to external 85% H_3PO_4 with downfield values reported as positive. Broad band and selective ^{1}H{^{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. ^{1}H,^{1}H 2D-COSY NMR experiments were conducted on the Bruker ACP 200 spectrometer.

4.2. Thermal isomerization of (triphos)Ir(H)$_2$(2-Tyl) (2) to (triphos)Ir(η^3-SCH = CH–CH = CH$_2$) (3)

A 5 mm NMR tube was charged under nitrogen with a solution of **2** (30 mg, 0.03 mmol) in either THF-d_8 or benzene-d_6 (0.7 ml), flame sealed and kept at 130 °C (oil bath). After 2 h, the tube was cooled to room temperature. ^{1}H and ^{31}P{^{1}H} NMR spectra of this sample showed the selective conversion of **2** to **3** (46:54 ratio based on ^{31}P{^{1}H} NMR integration of well-separated absorptions of the two complexes [2]). Although at a much lower rate, the reaction already occurs at 110 °C (conversion 5% in 2 h). No trace of either deutcrated isotopomers of (triphos)Ir(H)$_2$(C$_6$H$_5$) (**4**) or THF C–H bond activation products was detected [14].

4.3. Reaction of (triphos)Ir(H)$_2$(C$_2$H$_5$) (1) with BT

4.3.1. NMR experiment

A 5 mm NMR tube was charged with a mixture of (triphos)Ir(H)$_2$(C$_2$H$_5$) (**1**) (25 mg, 0.03 mmol) and **BT** (40 mg, 0.30 mmol) in THF-d_8 (0.8 ml) under nitrogen, flame-sealed and placed into the probe of a NMR spectrometer preheated to 67 °C. The reaction was followed with the use of ^{31}P{^{1}H} NMR spectroscopy by determining the concentrations of both **1** and the products as a function of time; spectra were recorded every hour. After 1 h, in addition to the starting complex (59%), two other products were observed in a ratio of 36:5. The major product was identified as (triphos)IrH(η^2-*C,S*-C$_8$H$_6$S) (**7**) [3] and the second product was identified as the C–H bond activation product [(triphos)Ir(H)$_2$(2-BTyl)] (**5**, BTyl = benzo[*b*]thienyl) by comparison with an authentic sample (see below). With time, **1** gradually disappeared, while **7** slowly converted to (triphos)Ir(η^3-S(C$_6$H$_4$)CH = CH$_2$) (**6**) [3]. Conversion of > 90% was achieved after ca. 5 h with the following product distribution: **7** (24%), **5** (13%), **6** (63%). After ca. 24 h, only **5** (13%) and **6** (87%) were detected in solution.

4.3.2. Synthetic experiment

A mixture of **1** (0.25 g, 0.30 mmol) and **BT** (0.40 g, 3.00 mmol) in THF (80 ml) was heated at reflux temperature for ca. 24 h. After the solvent was removed in vacuo, the yellow solid residue was washed three times with *n*-pentane (60 ml). NMR analysis showed this product to be a mixture of **5** and **6** in a ratio of 13 to 87. This product distribution did not change with time in the temperature range from 67 to 100 °C.

4.4. Independent synthesis of (triphos)Ir(H)$_2$(2-BTyl) (5)

Following a literature procedure for the synthesis of 2-benzo[*b*]thienyllithium [17], a 1.6 M solution of *n*-butyllithium in *n*-hexanes (0.72 ml, 1.15 mmol) was added to a solution of **BT** (0.154 g, 1.15 mmol) in THF (30 ml) cooled at 0 °C. After the solution was allowed to warm to room temperature, with stirring, for 30 min, the solution was refluxed for an additional 30 min and cooled to room temperature. To this stirred solution was added a sample of (triphos)Ir(H)$_2$Cl (0.20 g, 0.23 mmol) dissolved in THF (30 ml). After 3 h the resulting solution was concentrated to dryness and the residue treated with ethanol (5 ml). Addition of *n*-heptane (30 ml) led to the precipitation of pale yellow crystals of **5**, which were recrystallized twice from THF/*n*-heptane; yield 65%. Anal. Calc. for C$_{49}$H$_{46}$IrP$_3$S: C, 61.81; H, 4.87; Ir, 20.19; S, 3.37. Found: C, 61.12; H, 4.83; Ir, 20.01; S, 3.23. IR: ν(Ir-H) 2055 (m) cm^{-1}. ^{31}P{^{1}H} NMR (THF-d_8, 20 °C): AM$_2$ spin system, δ −7.9, t, ^2J(PP) = 15.8 Hz, P$_A$; −22.6, d, P$_M$. ^{1}H NMR (THF-d_8, 20 °C): δ 5.94, dd, ^4J(HP) = 3.3, 0.7, H$_3$; −8.76, second order doublet of multiplets, AA′XX′Y spin system, $|^2J(HP_M) + {}^2J(HP_{M'})|$ = 125.3 Hz, ^2J(HP$_A$) = 13.3 Hz, Ir-H.

4.5. Thermal isomerization of (triphos)Ir(H)$_2$(2-BTyl) (5) to (triphos)Ir(η^3-S(C$_6$H$_4$)CH = CH$_2$) (6)

A 5 mm NMR tube was charged under nitrogen with a solution of **5** (30 mg, 0.03 mmol) in either THF-d_8 or benzene-d_6 (0.7 ml), flame sealed and kept at 130 °C (oil bath). After 2 h, the tube was cooled to room temperature. ^{1}H and ^{31}P{^{1}H} NMR spectra of this sample showed the clean, although partial, conversion of **5** to **6** (10%). Very low conversion was observed at 110

°C (ca. 2% in 2 h). As in the case of the **2** to **3** isomerization, no trace of either deuterated isotopomers of (triphos)Ir$(H)_2(C_6H_5)$ (**4**) or THF C–H bond activation products was detected [14].

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