

# C–H Bond Cleavage in Thiophenes by [P(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>Ru]. UV Flash Kinetic Spectroscopy Discloses the Ruthenium–Thiophene Adduct Which Precedes C–H Insertion

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Received May 12, 1997<sup>®</sup>

Photolysis of [(PP<sub>3</sub>)RuH<sub>2</sub>] (PP<sub>3</sub> = P(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>) (**1**) in THF at 23 °C under an inert atmosphere (N<sub>2</sub>, Ar, or He) in the presence of thiophene (**T**) or ethyl 2-thiophenecarboxylate (2-CO<sub>2</sub>Et**T**) gives the (hydride)2-thienyl complexes [(PP<sub>3</sub>)Ru(H)(2-Tyl)] (**5**) (Tyl = C<sub>4</sub>H<sub>3</sub>S) and [(PP<sub>3</sub>)Ru(H)(2-CO<sub>2</sub>EtTyl)] (**7**) (CO<sub>2</sub>EtTyl = C<sub>4</sub>H<sub>2</sub>(CO<sub>2</sub>Et)S), respectively. The C–H insertion products **5** and **7** are also selectively obtained by the thermal reaction of the Ru(0) dinitrogen complex [(PP<sub>3</sub>)Ru(N<sub>2</sub>)] (**4**) in THF with **T** or 2-CO<sub>2</sub>Et**T**. Complexes **5** and **7** are both photochemically and thermally stable. Under comparable conditions, the photolysis of the Os derivative [(PP<sub>3</sub>)OsH<sub>2</sub>] in THF in the presence of **T** exclusively yields the C–H insertion product [(PP<sub>3</sub>)Os(H)(2-Tyl)]. Photolysis of **1** at 23 °C under nitrogen and in the presence of 2,5-dimethylthiophene (2,5-Me<sub>2</sub>**T**) gives the complex [(PP<sub>3</sub>)Ru(η<sup>1</sup>-S-2,5-Me<sub>2</sub>**T**)] (**8**) containing an S-bound thiophene molecule. Complex **8** is also obtained by reaction of isolated **4** with 2,5-Me<sub>2</sub>**T**. The Ru(0) transient, [(PP<sub>3</sub>)Ru], generated by laser flash photolysis in either cyclohexane or THF solution, has been detected and characterized by UV–vis spectroscopy. [(PP<sub>3</sub>)Ru] reacts with **T** ( $k_2 = (1.4 \pm 0.2) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ), yielding an adduct [(PP<sub>3</sub>)Ru(**T**)]. In cyclohexane, [(PP<sub>3</sub>)Ru(**T**)] decays to the C–H insertion product **5** with first-order kinetics ( $k = 20 \pm 1 \text{ s}^{-1}$  at 296 K). In THF, the 16 e<sup>-</sup> Ru(0) transient forms with THF a short-lived adduct, probably bound through oxygen, [(PP<sub>3</sub>)Ru(THF)], which reacts with **T** to give [(PP<sub>3</sub>)Ru(**T**)] ( $k_{\text{obs}} = 680 \text{ s}^{-1}$ , [**T**] = 0.3 mol dm<sup>-3</sup> under Ar). This **T** adduct decays to [(PP<sub>3</sub>)Ru(2-Tyl)H] with first-order kinetics ( $k = 18 \pm 1 \text{ s}^{-1}$ ). Similar measurements with 2,5-Me<sub>2</sub>**T** yield a rate constant for [(PP<sub>3</sub>)Ru] + 2,5-Me<sub>2</sub>**T** in cyclohexane of  $(1.0 \pm 0.3) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . The resulting [(PP<sub>3</sub>)Ru(2,5-Me<sub>2</sub>**T**)] is kinetically stable. Flash photolysis of [(PP<sub>3</sub>)OsH<sub>2</sub>] in cyclohexane with added **T** yields rate constants for [(PP<sub>3</sub>)Os] + **T** and for isomerization of [(PP<sub>3</sub>)Os(**T**)] of  $(3.7 \pm 0.1) \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $8 \pm 1 \text{ s}^{-1}$ , respectively.

## Introduction

Hydrodesulfurization (HDS) is a stepwise reaction of paramount industrial and environmental relevance whose mechanism(s), however, is still poorly understood.<sup>2</sup> In this process, sulfur, contained in various organic compounds such as thiols, sulfides, disulfides, and the more refractory thiophenic molecules, is removed from fossil materials upon treatment with H<sub>2</sub> in the presence of heterogeneous catalysts.

Homogeneous modeling studies have recently contributed several mechanistic breakthroughs regarding most of the steps which may be involved in the metal-assisted HDS of thiophenes to H<sub>2</sub>S and hydrocarbons.<sup>3</sup> However, the structure of the initial metal-intact thiophene adduct and the factors which control its

conversion to either C–S or C–H insertion products have hardly been studied. In part, the scarcity of information on this primary step is due to the stability of the detected or isolated metal–thiophene adducts with respect to their conversion to C–S or C–H insertion products.<sup>4</sup> On the other hand, the known C–S and C–H insertion reactions<sup>5</sup> occur so rapidly that the intermediacy of metal–thiophene adducts has only been postulated on the basis of theoretical<sup>6</sup> or indirect experimental evidence.<sup>5n</sup>

Among the authenticated bonding modes of thiophene (or substituted thiophenes) to metal centers (Chart 1), the η<sup>1</sup>-S (**I**)<sup>4a–k</sup> and η<sup>2</sup>-C,C (**II**)<sup>4l–o</sup> ones are believed to feature the immediate precursors to C–S and C–H bond cleavage, respectively.<sup>5c,n</sup> The η<sup>5</sup> (**III**) and η<sup>4</sup> (**IV**) coordination modes may also lead to C–S insertion by metal complexes,<sup>3</sup> but subsequent intra- or intermo-

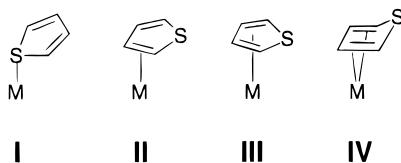
<sup>®</sup> Abstract published in *Advance ACS Abstracts*, September 15, 1997.

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Chart 1



lecular attack by either nucleophilic or electrophilic reagents is required.<sup>7</sup>

If it is taken for granted that C–S and C–H insertions, when they occur, are preceded by thiophene coordination, then the nondetection of intermediates is a kinetic question exclusively determined by the short lifetime of these species. Accordingly, fast kinetic techniques such as UV or IR flash kinetic spectroscopy, never applied to HDS modeling studies, might be the methods of choice for detecting the intermediates prior to C–S or C–H bond scission, as well as providing structural and kinetic information on the intermediate itself and its products.

Following the synthesis of [(PP<sub>3</sub>)RuH<sub>2</sub>] (**1**),<sup>8</sup> we have recently demonstrated that photolysis of **1** results in

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dissociation of H<sub>2</sub> and formation of products of the types [(PP<sub>3</sub>)RuL] (L = CO, N<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>) and [(PP<sub>3</sub>)Ru(X)H] (X = Ph, Et<sub>3</sub>Si) according to the substrate provided (PP<sub>3</sub> = P(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>). The reaction intermediate, [(PP<sub>3</sub>)Ru], was detected by laser flash photolysis, and the kinetics of its reactions with these substrates were measured.<sup>9</sup> The photochemistry of [(PP<sub>3</sub>)OsH<sub>2</sub>]<sup>10</sup> proceeds analogously, but oxidative addition occurs with THF and with alkanes.<sup>9</sup>

In this work, photolysis of [(PP<sub>3</sub>)RuH<sub>2</sub>]<sup>8</sup> is employed to generate the transient [(PP<sub>3</sub>)Ru] species in solution for reactions with selected thiophenes such as thiophene (**T**), ethyl 2-thiophenecarboxylate (2-CO<sub>2</sub>Et**T**), and 2,5-dimethylthiophene (2,5-Me<sub>2</sub>**T**). Monitoring these reactions by NMR spectroscopy shows that C–H insertion occurs for **T** and 2-CO<sub>2</sub>Et**T** to give (hydride)2-thienyl complexes with no detectable intermediates. In contrast, a Ru–**T** adduct is seen by laser flash photolysis with UV–vis detection, which also allows the quantification of reaction kinetics. We also include brief reports of the chemistry of the osmium analogues.

## Experimental Section

**General Information.** Tetrahydrofuran (THF) was purified by distillation under nitrogen over LiAlH<sub>4</sub>, and *n*-heptane was distilled over sodium. The solvents were stored over molecular sieves. Commercial thiophene (Aldrich, 99%) was purified as described in the literature.<sup>11</sup> All of the other reagents and chemicals, including ethyl 2-thiophenecarboxylate, were reagent grade and, unless otherwise stated, were used as received by commercial suppliers. All reactions and manipulations were routinely performed under a dry nitrogen, argon, or helium atmosphere using Schlenk tube techniques. The solid complexes were collected on sintered-glass frits and washed with ethanol and petroleum ether (bp 40–70 °C) before being dried in a stream of nitrogen. Literature methods were used for the preparation of [(PP<sub>3</sub>)RuH<sub>2</sub>] (**1**),<sup>8</sup> [(PP<sub>3</sub>)RuCl<sub>2</sub>] (**2**),<sup>8</sup> [(PP<sub>3</sub>)OsH<sub>2</sub>] (**3**),<sup>10</sup> and [(PP<sub>3</sub>)Ru(N<sub>2</sub>)] (**4**).<sup>9</sup> Photochemical reactions were performed by using a Helios Italquartz UV 13F apparatus. The photolysis source was a 135 W (principal emission wavelength at 366 nm) high-pressure mercury vapor immersion lamp equipped with a water filter to remove excess heat. Photolysis NMR experiments were carried out in 5 mm quartz NMR tubes (Wilmad 507-PP-QTZ). Deuterated solvents for NMR measurements (Merck) were dried over molecular sieves (4 Å). <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on a Varian VXR 300, Bruker AC 200P, or Bruker AVANCE DRX 500 spectrometer operating at 299.94, 200.13, or 500.13 MHz (<sup>1</sup>H) and 75.42, 50.32, or 125.80 MHz (<sup>13</sup>C), respectively. Peak positions are quoted relative to tetramethylsilane and were calibrated against the residual solvent resonance (<sup>1</sup>H) or the deuterated solvent multiplet (<sup>13</sup>C). <sup>13</sup>C-DEPT experiments were run on the Bruker AC 200P spectrometer. <sup>1</sup>H,<sup>13</sup>C-2D HETCOR NMR experiments were recorded on either the Bruker AC 200P spectrometer using the XHCORR pulse program or the Bruker AVANCE DRX 500 spectrometer equipped with a 5 mm triple-resonance probe head for <sup>1</sup>H detection and inverse detection of the heteronucleus (inverse correlation mode, HMQC experiment) with no sample spinning. The <sup>1</sup>H,<sup>1</sup>H-2D COSY NMR experiments

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were routinely conducted on the Bruker AC 200P instrument in the absolute magnitude mode using a 45° or 90° pulse after the incremental delay or were acquired on the AVANCE DRX 500 Bruker spectrometer using the gradient-accelerated version of the conventional COSY sequence (COSYPS). <sup>1</sup>H, <sup>1</sup>H-2D NOESY NMR experiments were conducted on the same instrument in the phase-sensitive TPPI mode in order to discriminate between positive and negative cross peaks. *T*<sub>1</sub> measurements for the optimization of the proper mixing time in the NOESY experiments were determined at 25 °C using the standard  $\pi$ - $\tau$ - $\pi/2$  inversion–recovery sequence. <sup>31</sup>P{<sup>1</sup>H} NMR spectra were acquired on the Varian VXR 300 or Bruker AC 200P instruments operating at 121.42 and 81.01, respectively. Chemical shifts were measured relative to external 85% H<sub>3</sub>PO<sub>4</sub> with downfield values taken as positive. The proton NMR spectra with broad-band phosphorus decoupling were recorded on the Bruker AC 200P instrument equipped with a 5 mm inverse probe and a BFX-5 amplifier device using the wide-band phosphorus decoupling sequence GARP. Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 1600 series FT-IR spectrophotometer between KBr plates. UV spectra were recorded at room temperature on a Shimadzu UV-2100 spectrophotometer using quartz cells. Elemental analyses (C, H, N) were performed using a Carlo Erba model 1106 elemental analyzer.

The laser flash photolysis apparatus in York has been described elsewhere.<sup>12</sup> In brief, a XeCl laser (308 nm) excites the sample, which is monitored by UV–vis absorption of light from a xenon arc lamp. The arc is pulsed for time scales up to 250  $\mu$ s. Samples were prepared in a 10 mm quartz cuvette, fitted with a PTFE stopcock and degassing bulb. Solid **1** or **3** was loaded into the cuvette in an argon-filled glovebox. Solvents were dried over CaH<sub>2</sub> at reflux and transferred to the flash cells via cannula on a Schlenk line fitted with a diffusion pump. The concentration was adjusted to obtain an absorbance of 0.6–1.0 at 308 nm before degassing the contents with three freeze–pump–thaw cycles and filling the cell with the required atmosphere. Measurements were made at 296  $\pm$  1 K.

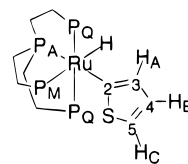
**Thermal Reaction of [(PP<sub>3</sub>)RuH<sub>2</sub>] with either Thiophene or Ethyl 2-Thiophenecarboxylate.** A solution of **1** (200 mg, 0.26 mmol) in neat thiophene (**T**) or ethyl 2-thiophenecarboxylate (2-CO<sub>2</sub>Et**T**) was gently heated under nitrogen to reflux. After 3 h of reflux, a 0.6 mL sample of the resulting orange solution was withdrawn and, after dilution with 0.4 mL of THF-*d*<sub>8</sub>, was analyzed by <sup>31</sup>P NMR spectroscopy. This showed no transformation of the starting dihydride. Identical results were obtained when **1** in THF was refluxed in the presence of variable amounts of either **T** or 2-CO<sub>2</sub>Et**T**.

**Photolysis of [(PP<sub>3</sub>)RuH<sub>2</sub>] in the Presence of Thiophene. A. NMR Experiment in THF-*d*<sub>8</sub>.** A solution of **1** (20 mg, 0.026 mmol) in THF-*d*<sub>8</sub> (0.6 mL) containing 100 equiv of **T** (0.21 mL, 2.60 mmol) prepared either under nitrogen or helium in a 5 mm quartz NMR tube was irradiated with UV light at 23 °C. Monitoring the photolysis reaction by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy every 10 min showed the exclusive formation of the (hydride)2-thienyl complex [(PP<sub>3</sub>)Ru(H)(2-Tyl)] (**5**) (Tyl = C<sub>4</sub>H<sub>3</sub>S). Complex **5** was the only product after 1 h of UV irradiation. At 60 °C, the photolysis of **1** with **T** led to the quantitative formation of **5** in a few minutes. Replacing THF-*d*<sub>8</sub> with benzene-*d*<sub>6</sub> did not change the reactivity.

**B. Bulk Photolysis in THF at Room Temperature.** A solution of **1** (200 mg, 0.26 mmol) in THF (10 mL) containing a large excess of **T** (5 mL, 62.40 mmol) was irradiated with UV light at 23 °C under nitrogen or helium. After 1 h, a 0.6 mL sample of the resulting orange solution was withdrawn and, after dilution with 0.4 mL of THF-*d*<sub>8</sub>, was analyzed by <sup>31</sup>P NMR spectroscopy. This showed that complete transformation of the starting dihydride into **5** had occurred.

### C. Bulk Photolysis in THF at Reflux Temperature.

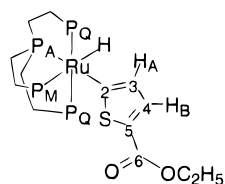
A solution of **1** (200 mg, 0.26 mmol) in THF (10 mL) containing a large excess of **T** (5 mL, 62.40 mmol) was irradiated under either nitrogen or helium with UV light without water cooling in a quartz flask connected to a reflux condenser. Within a few minutes, the solution reached the reflux temperature. After 30 min, the UV lamp was turned off and the yellowish reaction mixture was cooled to room temperature and then transferred into a Schlenk-flask under nitrogen. Addition of *n*-heptane (30 mL) and concentration of the resulting solution under a brisk current of nitrogen gave cream-colored microcrystals of **5**. Yield: 87%. IR:  $\nu$ (Ru–H) 1879 (m) cm<sup>-1</sup>. Anal. Calcd for C<sub>46</sub>H<sub>46</sub>P<sub>4</sub>RuS: C, 64.55; H, 5.42. Found: C, 64.27; H, 5.57. <sup>31</sup>P{<sup>1</sup>H} NMR (22 °C, C<sub>6</sub>D<sub>6</sub>, 81.01 MHz), AMQ<sub>2</sub> spin system:  $\delta$ <sub>A</sub> 146.09 (td, *J*<sub>AM</sub> = 6.8 Hz, *J*<sub>AQ</sub> = 13.1 Hz);  $\delta$ <sub>M</sub> 49.66 (td, *J*<sub>MQ</sub> = 12.4 Hz),  $\delta$ <sub>Q</sub> = 57.73 (dd). <sup>1</sup>H NMR (20 °C, C<sub>6</sub>D<sub>6</sub>, 500.13 MHz):  $\delta$ <sub>RuH</sub> -7.94 (dtd, *J*<sub>HPM</sub> = 81.0 Hz, *J*<sub>HPA</sub> = 15.2 Hz, *J*<sub>HPQ</sub> = 26.4 Hz);  $\delta$ <sub>HA</sub> 7.70 (brt, *J*<sub>HAPA</sub> = 2.7 Hz, *J*<sub>HAB</sub> = 3.0 Hz, *J*<sub>HCHC</sub> = 2.8 Hz);  $\delta$ <sub>HB</sub> 7.60 (dd, *J*<sub>HBC</sub> = 4.8 Hz);  $\delta$ <sub>HC</sub> 7.89 (brd). <sup>13</sup>C{<sup>1</sup>H} NMR (20 °C, THF-*d*<sub>8</sub>, 50.32 MHz):  $\delta$ <sub>C2</sub> 143.42 (brd, *J*<sub>CP</sub> = 21.9 Hz);  $\delta$ <sub>C3</sub> 140.02 (t, *J*<sub>CP</sub> = 6.0 Hz);  $\delta$ <sub>C4</sub> and  $\delta$ <sub>C5</sub> not observed (masked by the aromatic carbon resonances of PP<sub>3</sub>). Compound **5** is photochemically stable in THF solution up to reflux temperature.



**Reaction of [(PP<sub>3</sub>)Ru(N<sub>2</sub>)] with Thiophene.** A 5 mm screw-cap NMR tube was charged with a *ca.* 3  $\times$  10<sup>-2</sup> M solution of **4** (0.5 mL), freshly prepared by reduction of **2** with sodium naphthalenide in THF,<sup>9</sup> and with 0.5 mL of THF-*d*<sub>8</sub> under nitrogen. Then *ca.* 1.2 equiv of **T** was syringed into the solution through the serum cap, and a <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the solution was immediately acquired, which showed the partial conversion of **4** to **5** (30% after 1 h, based on <sup>31</sup>P NMR integration). Increasing the temperature of the spectrometer probe head to *ca.* 50 °C caused a fast fading of the red color of **4**, and the NMR analysis showed the complete transformation of **4** into **5**.

**Thermal Behavior of [(PP<sub>3</sub>)Ru(H)(2-Tyl)].** A solution of **5** (100 mg, 0.12 mmol) in *o*-xylene (bp 143–145 °C) was refluxed overnight under nitrogen. A <sup>31</sup>P{<sup>1</sup>H} NMR analysis showed no transformation of the starting material, which was recovered quantitatively.

**Photolysis of [(PP<sub>3</sub>)RuH<sub>2</sub>] in the Presence of Ethyl 2-Thiophenecarboxylate.** Substitution of 2-CO<sub>2</sub>Et for **T** in all the experiments described above gave identical results. From the preparative experiment **C**, the (hydride)2-thienyl complex [(PP<sub>3</sub>)Ru(H)(2-CO<sub>2</sub>EtTyl)] (**7**) was obtained in 90% yield (2-CO<sub>2</sub>EtTyl = C<sub>4</sub>H<sub>2</sub>(CO<sub>2</sub>Et)S). Compound **7** is thermally (up to 145 °C in *o*-xylene) and photochemically stable in solution. IR:  $\nu$ (Ru–H) 1902 (m) cm<sup>-1</sup>. Anal. Calcd for C<sub>49</sub>H<sub>50</sub>O<sub>2</sub>P<sub>4</sub>RuS: C, 63.42; H, 5.43. Found: C, 63.18; H, 5.50. <sup>31</sup>P{<sup>1</sup>H} NMR (20 °C, C<sub>6</sub>D<sub>6</sub>, 81.01 MHz), AMQ<sub>2</sub> spin system:  $\delta$ <sub>A</sub> 145.40 (td, *J*<sub>AM</sub> = 7.2 Hz, *J*<sub>AQ</sub> = 13.5 Hz);  $\delta$ <sub>M</sub> 50.53 (td, *J*<sub>MQ</sub> = 12.1 Hz; this resonance becomes a broad doublet in the proton-coupled <sup>31</sup>P NMR spectrum, *J*<sub>PHtrans</sub> = *ca.* 91 Hz);  $\delta$ <sub>Q</sub> 57.82 (dd). <sup>1</sup>H NMR (25 °C, C<sub>6</sub>D<sub>6</sub>, 500.13 MHz):  $\delta$ <sub>RuH</sub> -7.99 (dtd, *J*<sub>HPM</sub> = 90.6 Hz, *J*<sub>HPA</sub> = 15.4 Hz, *J*<sub>HPQ</sub> = 26.0 Hz);  $\delta$ <sub>HA</sub> 7.69 (dd, *J*<sub>HAPA</sub> = 2.1 Hz, *J*<sub>HAB</sub> = 3.6 Hz);  $\delta$ <sub>HB</sub> 8.41 (d);  $\delta$ <sub>OC<sub>2</sub>H<sub>5</sub>CH<sub>3</sub></sub> 4.36 (q, *J*<sub>HH</sub> = 7.0 Hz);  $\delta$ <sub>OC<sub>2</sub>H<sub>5</sub></sub> 1.21 (t). <sup>13</sup>C{<sup>1</sup>H} NMR (20 °C, C<sub>6</sub>D<sub>6</sub>, 50.32 MHz):  $\delta$ <sub>C6</sub> 166.90 (s),  $\delta$ <sub>C2</sub> 143.41 (td, *J*<sub>CP</sub> = 22.4, 6.2 Hz, assigned by a DEPT-NMR experiment),  $\delta$ <sub>C3</sub> 140.11 (t, *J*<sub>CP</sub> = 12.5 Hz, assigned by a 2D-<sup>1</sup>H, <sup>13</sup>C–HMQC NMR experiment),  $\delta$ <sub>C4</sub> *ca.* 132.8 (masked by the aromatic carbon resonances of PP<sub>3</sub>, assigned by a 2D-<sup>1</sup>H, <sup>13</sup>C–HMQC NMR experiment),  $\delta$ <sub>C5</sub> not observed (masked by the aromatic carbon resonances of PP<sub>3</sub>),  $\delta$ <sub>OC<sub>2</sub>H<sub>5</sub>CH<sub>3</sub></sub> 59.82 (s),  $\delta$ <sub>OC<sub>2</sub>H<sub>5</sub></sub> 15.41 (s).



**Photolysis of [(PP<sub>3</sub>)RuH<sub>2</sub>] in the Presence of 2,5-Dimethylthiophene. A. NMR Experiment in THF-*d*<sub>8</sub> under Nitrogen.** A 5 mm quartz NMR tube was charged under nitrogen with a mixture of **1** (20 mg, 0.026 mmol) and 2,5-dimethylthiophene (2-Me<sub>2</sub>T) (0.5 mL) in 0.5 mL of THF-*d*<sub>8</sub>. The tube was irradiated with UV light at 23 °C. Monitoring the photolysis reaction by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy showed the partial conversion of **1** to several products. After 3 h, the following product composition was determined by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy: **1** (12%), **4** (26%), [(Ph<sub>2</sub>PCH<sub>2</sub>-CH<sub>2</sub>)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh(C<sub>6</sub>H<sub>4</sub>)}RuH] (**6**)<sup>9</sup> (10%), [(PP<sub>3</sub>)Ru(C<sub>4</sub>H<sub>2</sub>-Me<sub>2</sub>S)] (**8**) (40%), unidentified products (12%). <sup>31</sup>P{<sup>1</sup>H} NMR of **8** (20 °C, THF-*d*<sub>8</sub>, 81.01 MHz): AM<sub>3</sub> spin system: δ<sub>A</sub> 162.25 (q, *J*<sub>AM</sub> = 23.6 Hz); δ<sub>M</sub> 65.26 (d).

**B. NMR Experiment in THF-*d*<sub>8</sub> under Helium.** A solution of **1** (20 mg, 0.026 mmol) in a THF-*d*<sub>8</sub>/2,5-Me<sub>2</sub>T mixture (1.0 mL, 1:1 v/v) prepared under helium in a 5 mm quartz NMR tube was irradiated with UV light at 23 °C. After 1 h of photolysis, NMR analysis gave the following product composition: **1** (17%), **6** (20%), **8** (48%), unidentified products (15%).

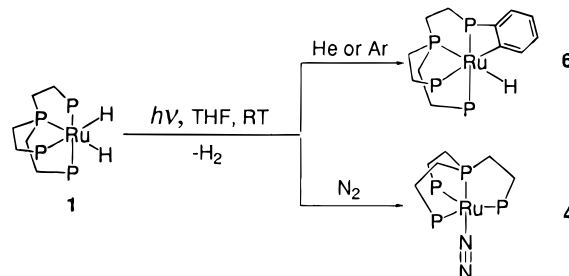
**C. NMR Experiment in Neat 2,5-Dimethylthiophene.** A solution of **1** (20 mg, 0.026 mmol) in neat 2,5-Me<sub>2</sub>T (0.7 mL) prepared under helium in a 5 mm quartz NMR tube containing a sealed capillary with acetone-*d*<sub>6</sub> for the internal lock was irradiated with UV light at 23 °C. After 1 h, a <sup>31</sup>P{<sup>1</sup>H} NMR spectrum showed the complete disappearance of **1** with formation of **6** (12%) and **8** (48%) and other unidentified products.

**Reaction of [(PP<sub>3</sub>)Ru(N<sub>2</sub>)] with 2,5-Dimethylthiophene.** A 5 mm NMR tube was charged under nitrogen with 30 mg of **4** (0.043 mmol) and 0.7 mL of 2,5-Me<sub>2</sub>T (6.15 mmol) at room temperature. Monitoring the reaction by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy showed the slow transformation of **4** into **8**. After 12 h, an overall transformation of ca. 65% was observed. Prolonged reaction times (48 h) did not change the ratio between **8** and **4**. Any attempt to precipitate **8** from this dark red solution resulted in extensive decomposition and gave intractable sticky materials. Extensive decomposition was analogously observed when the solvent was removed in vacuo at room temperature. The resulting oily residue, however, still contained **8** (ca. 15%). A <sup>1</sup>H NMR spectrum in THF-*d*<sub>8</sub> was acquired, which showed the absence of resonances in the region from 3 to 5 ppm where the pseudo-olefinic hydrogens of η<sup>2</sup>-*C,C*-thiophenes are known to resonate.<sup>41,m,o</sup> We thus assign **8** as [(PP<sub>3</sub>)Ru(η<sup>1</sup>-*S*-C<sub>4</sub>H<sub>2</sub>Me<sub>2</sub>S)] (δ<sub>Me</sub> 2.20). In an independent experiment, the reaction mixture was transferred under nitrogen into a quartz cuvette. The UV spectrum showed an absorption maximum centered at 400 nm.

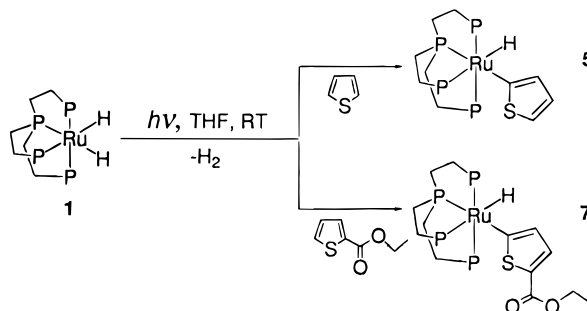
**Photolysis of [(PP<sub>3</sub>)OsH<sub>2</sub>] (3) in the Presence of Thiophene. A. NMR Experiment in THF-*d*<sub>8</sub>.** A solution of **3**<sup>10</sup> (20 mg, 0.023 mmol) in THF-*d*<sub>8</sub> (0.6 mL) containing 100 equiv of **T** (0.21 mL, 2.60 mmol) prepared under nitrogen in a 5 mm quartz NMR tube was irradiated with UV light at 23 °C. Monitoring the photolysis reaction by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy showed the quantitative formation of the (hydride)2-thienyl complex [(PP<sub>3</sub>)Os(H)(2-Tyl)] (**9**) after 30 min.

**B. Bulk Photolysis in THF-*d*<sub>8</sub> at Room Temperature.** A solution of [(PP<sub>3</sub>)OsH<sub>2</sub>] (**3**) (200 mg, 0.23 mmol) in THF (10 mL) containing a large excess of **T** (5 mL, 62.40 mmol) was photolyzed in a quartz flask at room temperature. Within a few minutes, the solution became pale orange. After 1 h of photolysis, the orange solution was transferred into a Schlenk-flask under nitrogen. Addition of *n*-heptane (30 mL) and concentration of the resulting solution under a brisk current

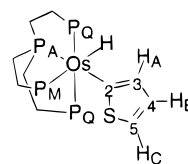
### Scheme 1



### Scheme 2



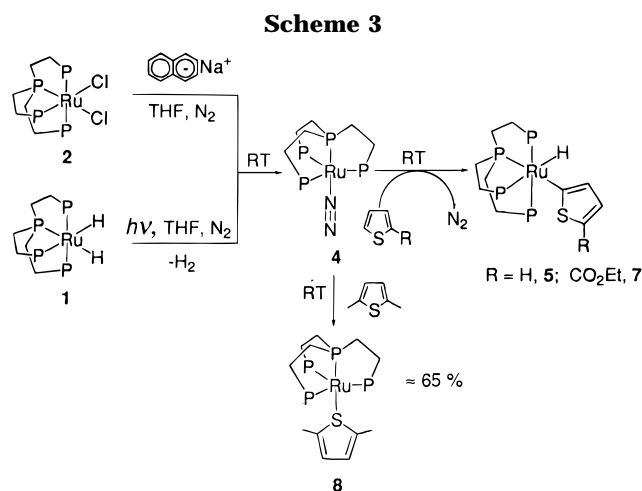
of nitrogen gave pale yellow microcrystals of the (hydride)2-thienyl complex **9**. Yield: 80%. IR: ν(Os-H) 2092 (m) cm<sup>-1</sup>. Anal. Calcd for C<sub>46</sub>H<sub>46</sub>OsP<sub>4</sub>S: C, 58.46; H, 4.91. Found: C, 58.21; H, 5.06. <sup>31</sup>P{<sup>1</sup>H} NMR (22 °C, C<sub>6</sub>D<sub>6</sub>, 121.42 MHz) AMQ<sub>2</sub> spin system: δ<sub>A</sub> 120.96 (d, *J*<sub>AM</sub> = 6.4 Hz, *J*<sub>AQ</sub> ≈ 0 Hz); δ<sub>M</sub> 21.41 (d, *J*<sub>MQ</sub> = 4.9 Hz); δ<sub>Q</sub> 22.33 (dt). <sup>1</sup>H NMR (20 °C, C<sub>6</sub>D<sub>6</sub>, 200.13 MHz): δ<sub>OsH</sub> -8.98 (dtd, *J*<sub>HPM</sub> = 76.2 Hz, *J*<sub>HPA</sub> = 9.5 Hz, *J*<sub>HPQ</sub> = 27.4 Hz); δ<sub>HA</sub> 7.14 (brd, *J*<sub>HAHB</sub> = 4.6 Hz); δ<sub>HB</sub> 6.74 (dd, *J*<sub>HBHC</sub> = 3.2 Hz); δ<sub>Hc</sub> ca. 7.0 (masked by the aromatic proton resonances of PP<sub>3</sub>, assigned by a <sup>1</sup>H, <sup>1</sup>H-2D COSY NMR experiment).



## Results

**Synthesis and Characterization of [(PP<sub>3</sub>)M(H)-(2-thienyl)] (M = Ru, thienyl = C<sub>4</sub>H<sub>3</sub>S (**5**); M = Ru, thienyl = C<sub>4</sub>H<sub>2</sub>(CO<sub>2</sub>Et)S (**7**); M = Os, thienyl = C<sub>4</sub>H<sub>3</sub>S (**9**)).** Photolysis (290 nm < λ < 376 nm) of [(PP<sub>3</sub>)RuH<sub>2</sub>] (**1**) in THF under an atmosphere of nitrogen has recently been reported to give the trigonal-bipyramidal dinitrogen adduct [(PP<sub>3</sub>)Ru(N<sub>2</sub>)] (**4**),<sup>9</sup> occasionally contaminated by the ortho-metalated complex [(Ph<sub>2</sub>PCH<sub>2</sub>-CH<sub>2</sub>)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh(C<sub>6</sub>H<sub>4</sub>)}RuH] (**6**) (*vide infra*). The latter compound is selectively formed when the photochemical reaction is carried out under He or Ar (Scheme 1).<sup>9</sup>

Neither compound **4** nor **6** forms when the photolysis of **1** is carried out at room temperature in the presence of either **T** or 2-CO<sub>2</sub>EtT either under N<sub>2</sub> or He. In contrast, these photochemical reactions exclusively yield the (hydride)2-thienyl complexes [(PP<sub>3</sub>)Ru(H)(2-Tyl)] (**5**) (Tyl = C<sub>4</sub>H<sub>3</sub>S) and [(PP<sub>3</sub>)Ru(H)(2-CO<sub>2</sub>EtTyl)] (**7**) (CO<sub>2</sub>-EtTyl = C<sub>4</sub>H<sub>2</sub>(CO<sub>2</sub>Et)S), resulting from the regioselective insertion of Ru into the α-C-H bond of the thiophenes (Scheme 2). Monitoring the photolysis reactions by NMR spectroscopy in quartz tubes shows that the conversion of **1** to the 2-thienyl products proceeds



with no detectable intermediates. Experiments at significantly lower temperatures ( $<0\text{ }^{\circ}\text{C}$ ) showed reduced conversion to **1** but no intermediate species.

Consistent with the photochemical reactions under  $\text{N}_2$ , the dinitrogen adduct **4** in THF is not stable in the presence of **T** or 2- $\text{CO}_2\text{EtT}$  and transforms into the corresponding (hydride)<sub>2</sub>-thienyl compounds (Scheme 3). Monitoring the thermal reactions between **4** and the thiophenes by  $^{31}\text{P}$  NMR spectroscopy shows slow conversion at room temperature and rapid reaction at  $50\text{ }^{\circ}\text{C}$ . No intermediates are observed prior to C–H bond cleavage.

Once formed, the thienyl complexes **5** and **7** are photochemically and thermally (up to  $145\text{ }^{\circ}\text{C}$ ) stable under an inert atmosphere. Cleavage of the C–S bond to give metallathiacycles does not occur even for **7** in which the electron-withdrawing carboxy substituent in the thienyl ligand might stabilize the transition state to C–S insertion.<sup>5b</sup>

The identification of **5** and **7** as *cis*-(hydride)<sub>2</sub>-thienyl complexes has been achieved unambiguously by NMR spectroscopy. In particular, the  $^{31}\text{P}$  and the hydride regions of the  $^1\text{H}$  NMR spectra are fully comparable with those of related *cis*-(hydride) $\sigma$ -organyl complexes such as  $[(\text{PP}_3)\text{RuH}(\text{C}\equiv\text{CPh})]$  and  $[(\text{PP}_3)\text{RuH}\{\text{MeO}_2\text{C}\text{C}=\text{CH}(\text{CO}_2\text{Me})\}]$ , which exhibit octahedral coordination geometries (where the terminal hydride and the organyl ligand, *trans* to the bridgehead phosphorus donor, are mutually *cis*).<sup>13</sup> For this reason, a detailed account of these spectra is not given here. In contrast, it is worth commenting on the regiochemistry of the C–H insertion, which has been determined unequivocally by plain  $^1\text{H}$  NMR spectroscopy for **5** and by 2D- $^1\text{H}$ , $^1\text{H}$  phase-sensitive NOESY spectroscopy for **7**.

For **T**, C–H insertion may occur at the 2- or 3-position to give regioisomers **V** and **VI**,<sup>5k,n</sup> while three regioisomers (**VII**–**IX**) are possible for 2- $\text{CO}_2\text{EtT}$  due to insertion into three chemically inequivalent C–H bonds (Chart 2). The pattern observed for the three thienyl proton resonances in the  $^1\text{H}\{^{31}\text{P}\}$  NMR spectrum of **5** (two doublets and a doublet of doublets) is exclusively consistent with the assignment as a 2-thienyl complex. Indeed, although examples of C–H cleavage at the 3-carbon atom are known,<sup>5k,n</sup> the predominant reactivity

of **T** occurs at the carbon atom adjacent to, and activated by, the sulfur atom.<sup>4a,5k,n</sup> From the  $^1\text{H}\{^{31}\text{P}\}$  NMR spectrum of **7** one can exclude the formation of regioisomer **VIII** which should contain two singlets for the thienyl C–H protons. The observation in the  $^1\text{H}$  NMR spectrum of a doublet at 8.41 ppm and of a doublet of doublets at 7.69 ppm (this collapses to a doublet with  $J_{\text{H}_A\text{H}_B} = 3.6\text{ Hz}$  in the  $^1\text{H}\{^{31}\text{P}\}$  spectrum) does not discriminate, however, between structures **VII** and **IX** resulting from insertion at the 2- and 4-positions. These two regioisomers would exhibit similar  $^1\text{H}$  NMR patterns for the thienyl protons, while the electron-withdrawing character of the  $\text{CO}_2\text{Et}$  substituent might balance the sulfur atom for the activation of the proximal C–H group.

Successful discrimination between regioisomers **VII** and **IX** has been achieved by looking at the spatial relationships between the hydride ligand and the thienyl protons with 2D- $^1\text{H}$ , $^1\text{H}$  phase-sensitive NOESY spectroscopy ( $\tau_{\text{mix}} = 1100\text{ ms}$ ) after the complete proton network in the complex had been assigned through a combination of 1D- and 2D-NMR experiments (see Experimental Section). The essential information obtained from the NOESY phase-sensitive correlation experiment is summarized in Figure 1.

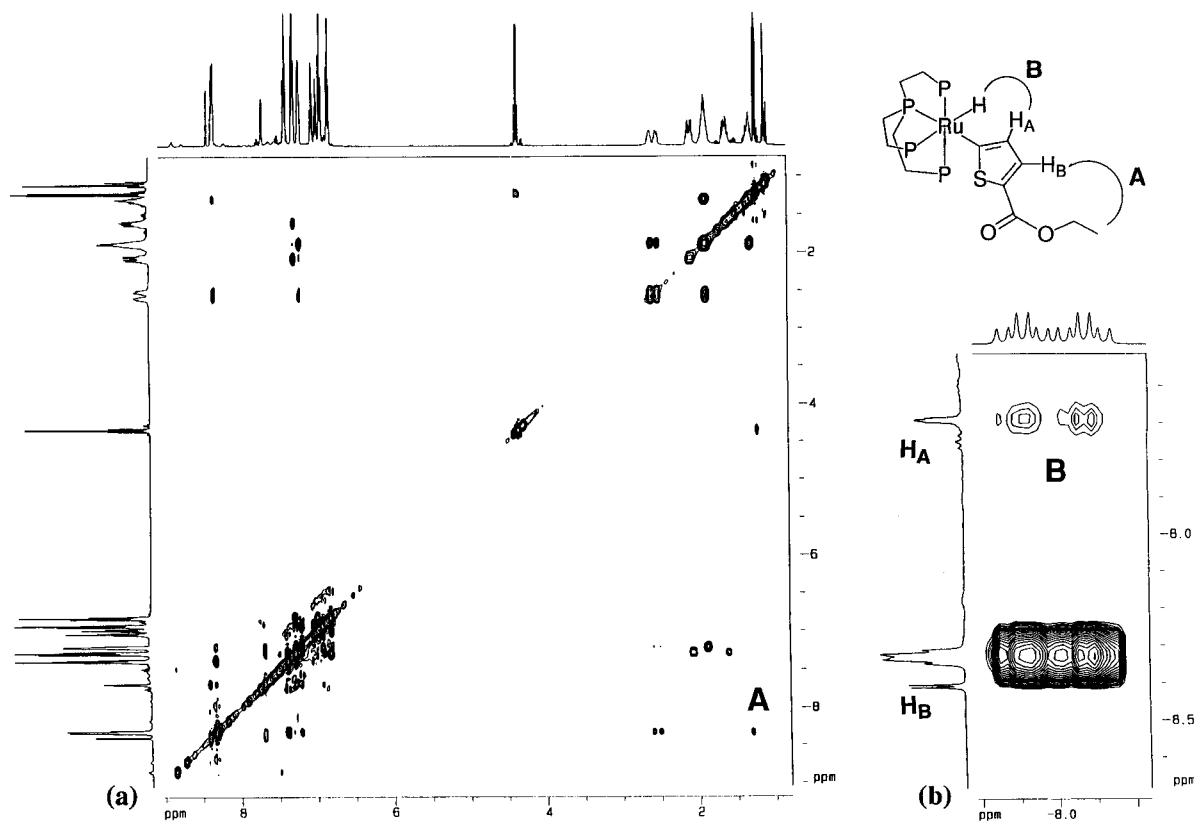
The most diagnostic NOE contacts are those between the methyl protons of the  $\text{CO}_2\text{Et}$  group and only one of the two thienyl protons,  $\text{H}_B$  (cross peak **A**), and between the hydride atom and the other thienyl proton,  $\text{H}_A$  (cross peak **B**). Consistently, the other thienyl proton,  $\text{H}_B$ , does not show any NOE contact to the terminal hydride. Additional evidence in favor of structure **VII** is provided by the absence of any dipolar interaction between the hydride resonance and the protons of the  $\text{CO}_2\text{Et}$  group.

Identical regioselectivity of C–H insertion, as well as overall complex structure, is observed when transient  $[(\text{PP}_3)\text{Os}]$ , photolytically generated in THF from  $[(\text{PP}_3)\text{OsH}_2]$ ,<sup>10</sup> is reacted with **T** (Scheme 4). The resulting (hydride)<sub>2</sub>-thienyl complex  $[(\text{PP}_3)\text{Os}(\text{H})(2\text{-Tyl})]$  (**9**) exhibits spectroscopic characteristics (NMR, IR) which are fully comparable with those of the Ru derivative **5** (see Experimental Section).

**Synthesis and Characterization of the  $\eta^1\text{-S-2,5-Dimethylthiophene Complex } [(\text{PP}_3)\text{Ru}(\eta^1\text{-S-C}_4\text{H}_2\text{Me}_2\text{S})]$ .** Photolysis of **1** in THF in the presence of a large excess of 2,5- $\text{Me}_2\text{T}$  (100 equiv) for 3 h under a nitrogen atmosphere gives partial conversion of the dihydride complex to a mixture of products among which the most abundant (40%) is a new species that we assign

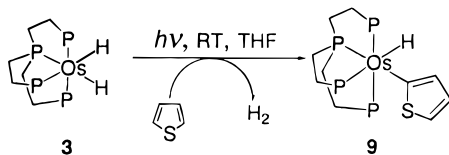
(13) Bianchini, C.; Frediani, P.; Masi, D.; Peruzzini, M.; Zanobini, F. *Organometallics* **1994**, *13*, 4616.

(14) Myers, A. W.; Jones, W. D.; McClements, S. M. *J. Am. Chem. Soc.* **1995**, *117*, 11704.



**Figure 1.** (a) Section of the phase-sensitive 2D- $^1\text{H}$  NOESY spectrum of **7** (500.13 MHz,  $\text{C}_6\text{D}_6$ , 25  $^\circ\text{C}$ ,  $\tau_{\text{mix}} = 1100$  ms) showing the negative cross peak (**A**) between the methyl protons of the  $\text{CO}_2\text{Et}$  group and the proton  $\text{H}_\text{B}$  of the thienyl group. (b) Contour plot of a section of the same spectrum showing the close contact (**B**) between the hydride at  $\delta -7.99$  and the proton  $\text{H}_\text{A}$  of the thienyl group.

#### Scheme 4



as  $[(\text{PP}_3)\text{Ru}(\eta^1\text{-}S\text{-C}_4\text{H}_2\text{Me}_2\text{S})]$  (**8**) (*vide infra*). The other products are the dinitrogen complex **4** (26%), the *o*-metalated complex **6** (10%), and some unidentified products (12%). Under a helium atmosphere, the photochemical reaction is faster and produces **8** and **6** together with some unidentified products. After 1 h, the following product distribution was determined by  $^{31}\text{P}$  NMR integration: **6**, 20%; **8**, 48%; unidentified products, 15%. A similar product distribution was also observed in neat 2,5- $\text{Me}_2\text{T}$  as the solvent.

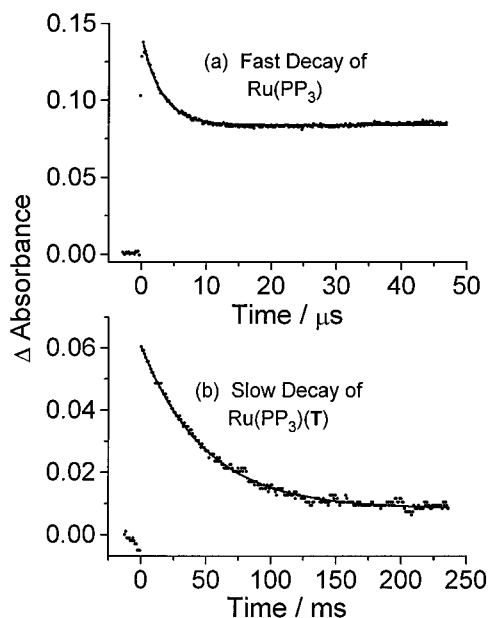
A more selective and cleaner reaction occurs when isolated **4** is dissolved in neat 2,5- $\text{Me}_2\text{T}$  under nitrogen at room temperature (NMR experiment), as only **8** is formed in *ca.* 65% yield after 12 h. Interestingly, the ratio between **4** and **8** does not change with time within 48 h (Scheme 3), which suggests the occurrence of an equilibrium mixture.

The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **8** consists of a temperature-invariant  $\text{AM}_3$  spin system with chemical shifts and coupling constants ( $\delta_\text{A}$  162.25 (q,  $J_{\text{AM}} = 23.6$  Hz);  $\delta_\text{M}$  65.26 (d)) which are typical of trigonal-bipyramidal  $(\text{PP}_3)\text{Ru}(0)$  complexes where the axial position *trans* to the bridgehead phosphorus is occupied by a neutral  $\sigma$ -donor (*e.g.*, **4** or  $[(\text{PP}_3)\text{Ru}(\text{CO})]$ ).<sup>9</sup> Although **8** could not be isolated in the solid state due to its instability, an oily residue, still containing *ca.* 15% of

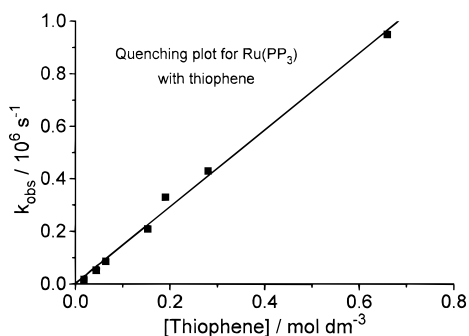
**8**, was obtained by removing the excess amount of 2,5- $\text{Me}_2\text{T}$  under reduced pressure. The  $^1\text{H}$  NMR spectrum in  $\text{THF-}d_8$  of the residue does not contain signals in the region from 3 to 5 ppm where the pseudo-olefinic protons of  $\eta^2\text{-}C,C$ -thiophenes, including  $\eta^2\text{-}2,5\text{-Me}_2\text{T}$ , are known to resonate.<sup>4l,m,o</sup> The UV-vis spectrum of the 35:65 mixture of **4** and **8** shows an absorption maximum at *ca.* 400 nm. Since isolated **4** absorbs at this wavelength,<sup>9</sup> one cannot assign the observed UV band exclusively to **8**, but the spectrum suggests that the predominant product **8** also absorbs at 400 nm. On the basis of the overall experimental evidence, we thus assign **8** as a trigonal-bipyramidal  $\text{Ru}(0)$  complex in which the axial position *trans* to the bridgehead P atom is occupied by an *S*-bound 2,5- $\text{Me}_2\text{T}$  molecule.

Thiophenes can bind 16-electron metal fragments through either the S atom or a C=C bond.<sup>4</sup> Equilibrium mixtures of  $\eta^1\text{-}S$  and  $\eta^2\text{-}C,C$  isomers have also been observed.<sup>4n,o</sup> It is generally agreed that alkyl substituents in the thiophene favor  $\eta^1\text{-}S$  coordination by a synergic effect: the alkyl substituents enhance both the basicity of the S atom and the steric hindrance at the C=C bonds.<sup>4d,e</sup> In the specific case of 2,5- $\text{Me}_2\text{T}$ , only one example of  $\eta^2\text{-}C,C$  coordination has been reported, *i.e.*,  $[\text{Os}(\text{NH}_3)_5(2,5\text{-Me}_2\text{T})]^{2+}$  where the supporting metal fragment is not sterically demanding at all,<sup>4l</sup> while  $\eta^1\text{-}S$  complexes are much more numerous.<sup>4</sup>

In conclusion, both electronic and steric factors may contribute to explain why 2,5- $\text{Me}_2\text{T}$  forms a stable  $\eta^1\text{-}S$  adduct with  $[(\text{PP}_3)\text{Ru}]$  while **T** or 2- $\text{CO}_2\text{EtT}$  do not: the two methyl substituents, in fact, enhance the donor ability of the sulfur atom and sterically congest the C-C double bonds.



**Figure 2.** (a) Transient decay of absorption monitored at 400 nm following laser flash photolysis (308 nm) of **1** in a cyclohexane solution in the presence of **T** ( $[\mathbf{T}] = 0.19 \text{ mol dm}^{-3}$ ). Notice the residual absorption of the product  $[(\text{PP}_3)\text{Ru}(\mathbf{T})]$ . (b) Decay in absorption of  $[(\text{PP}_3)\text{Ru}(\mathbf{T})]$  monitored on a millisecond time scale after generation as in a.



**Figure 3.** Plot of the pseudo-first-order rate constant for reaction of  $\text{Ru}(\text{PP}_3)$  with **T** versus  $[\mathbf{T}]$ .

**Laser Flash Photolysis Experiments.** Extensive experiments have recently shown that a transient species with  $\lambda_{\text{max}}$  395 nm is formed when **1**, dissolved in cyclohexane, is subjected to a laser flash at 308 nm.<sup>9</sup> In the absence of added reagents, the transient decays by first-order kinetics in *ca.* 20 ms. The transient, which is identified as the 16-electron  $\text{Ru}(0)$  complex  $[(\text{PP}_3)\text{Ru}]$ , reacts with a variety of reagents including  $\text{N}_2$ ,  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{C}_6\text{H}_6$ ,  $\text{C}_2\text{H}_4$ , and THF. The resulting second-order rate constants are all close to  $10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . The trigonal-bipyramidal  $\text{Ru}(0)$  products  $[(\text{PP}_3)\text{RuL}]$  ( $\text{L} = \text{N}_2, \text{THF}, \text{CO}, \text{C}_2\text{H}_4$ ) have absorption maxima in the region 400–440 nm.<sup>9</sup>

Laser flash photolysis experiments were carried out on solutions of **1** (*ca.*  $10^{-4} \text{ mol dm}^{-3}$ ) in cyclohexane containing **T** ( $0.02\text{--}0.15 \text{ mol dm}^{-3}$ ). The resulting  $[(\text{PP}_3)\text{Ru}]$  transient may be monitored at 400 nm and decays with pseudo-first-order kinetics with  $k_{\text{obs}}$  between  $1.77 \times 10^4$  and  $20.9 \times 10^4 \text{ s}^{-1}$  to yield  $[(\text{PP}_3)\text{Ru}(\mathbf{T})]$  (Figure 2a, see below). A plot of  $k_{\text{obs}}$  vs  $[\mathbf{T}]$  is linear (Figure 3) and yields a second-order rate constant of  $(1.4 \pm 0.2) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . The species  $[(\text{PP}_3)\text{Ru}(\mathbf{T})]$  has an absorption maximum at  $410 \pm 10 \text{ nm}$ , and itself decays with first-order kinetics with a rate constant of

$20 \text{ s}^{-1}$ , which varies by only *ca.* 5% over the range of **T** concentrations used (Figure 2b and Chart 3a). Neither fast nor slow rate constants were affected by replacement of the Ar atmosphere by  $\text{H}_2$  or  $\text{N}_2$ .

Flash photolysis of **1** in THF shows that transient  $[(\text{PP}_3)\text{Ru}]$  rapidly forms a short-lived solvent adduct in which THF probably binds the metal center through oxygen.<sup>9</sup> In the absence of quenchers,  $[(\text{PP}_3)\text{Ru}(\text{THF})]$  decays to form the cyclometalated complex **6** with  $k_{\text{obs}} = 5 \text{ s}^{-1}$ ,<sup>9</sup> while under  $\text{N}_2$  it converts to the dinitrogen complex **4** with a rate constant of  $50 \text{ s}^{-1}$ . Repetition of the experiment in THF with *ca.*  $0.3 \text{ mol dm}^{-3}$  **T** under Ar results in the conversion of  $[(\text{PP}_3)\text{Ru}(\text{THF})]$  to  $[(\text{PP}_3)\text{Ru}(\mathbf{T})]$  ( $k_{\text{obs}} = 680 \text{ s}^{-1}$ ,  $k_2 \approx 2.2 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ), which subsequently decays with a first-order rate constant of  $18 \text{ s}^{-1}$  (Chart 3b). The reactions were repeated under atmospheres of  $\text{H}_2$  and  $\text{N}_2$ , but neither fast nor slow decay rates were affected.

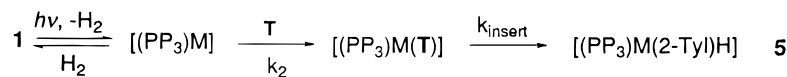
Similar laser flash photolysis experiments were carried out with **1** in a cyclohexane solution in the presence of 2,5-Me<sub>2</sub>**T** ( $0.1\text{--}0.34 \text{ mol dm}^{-3}$ ). The observed rate constant varied linearly with  $[\text{2,5-Me}_2\mathbf{T}]$ , yielding  $k_2 = (1.0 \pm 0.3) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . As with **T**, a considerable change in absorbance remained after the decay was complete. Unlike the thiophene case, however, no further decay was observed up to 1 s (the upper instrumental limit).

Laser flash photolysis measurements were also carried out with  $[(\text{PP}_3)\text{OsH}_2]$ , **3**, in cyclohexane in the presence of thiophene ( $0.39\text{--}0.93 \text{ mol dm}^{-3}$ ) under argon. The results paralleled those with **1**. Transient  $[(\text{PP}_3)\text{Os}]$ , monitored at 400 nm, reacted with thiophene in two sequential steps: (a) a fast decay process which was linearly dependent on thiophene concentration yielded  $k_2 = (3.7 \pm 0.1) \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , (b) a slower decay which was independent of  $[\mathbf{T}]$  with  $k_{\text{obs}} = 8 \pm 1 \text{ s}^{-1}$  (Chart 3a). The wavelength of maximum absorbance for the long-lived species was *ca.* 440 nm.

Identification of the product resulting from the reaction of transient  $[(\text{PP}_3)\text{Ru}]$  with **T** is possible by comparison with absorption spectra of related complexes and by consideration of the evidence from preparative experiments. Since the latter have shown that the C–H insertion product **5** is thermally stable, we can exclude this from consideration. Also, the absorption band at  $410 \pm 10 \text{ nm}$  is close to those of several trigonal-bipyramidal  $(\text{PP}_3)\text{Ru}(0)$  complexes containing a neutral ligand in the apical position *trans* to the bridgehead phosphorus (*vide supra*).<sup>9</sup> We therefore assign this species as  $[(\text{PP}_3)\text{Ru}(\mathbf{T})]$  (**10**), where **T** binds the metal center through either the sulfur atom or a C=C bond.<sup>4</sup> Indeed, the first-order decay of **10** fits isomerization to the C–H insertion product, **5**, the product observed in steady-state experiments. The alternative pathway of reversible dissociation of **T**, followed by cyclometalation of the  $[(\text{PP}_3)\text{Ru}]$  fragment to give **6** (rate constant  $350 \text{ s}^{-1}$ ),<sup>9</sup> should yield an inverse dependence on  $[\mathbf{T}]$ . Just such behavior was observed in the reaction of  $[(\text{PP}_3)\text{Ru}]$  with THF in cyclohexane.<sup>9</sup> The observations made in the presence of 2,5-Me<sub>2</sub>**T** are also consistent with the steady-state measurements. The initial product, assigned as  $[(\text{PP}_3)\text{Ru}(2,5\text{-Me}_2\mathbf{T})]$ , shows no further decay in keeping with the NMR observation that this is a stable complex. The rate constant for the reaction of  $[(\text{PP}_3)\text{Ru}] + 2,5\text{-Me}_2\mathbf{T}$  is similar to that with **T**. We have

## Chart 3

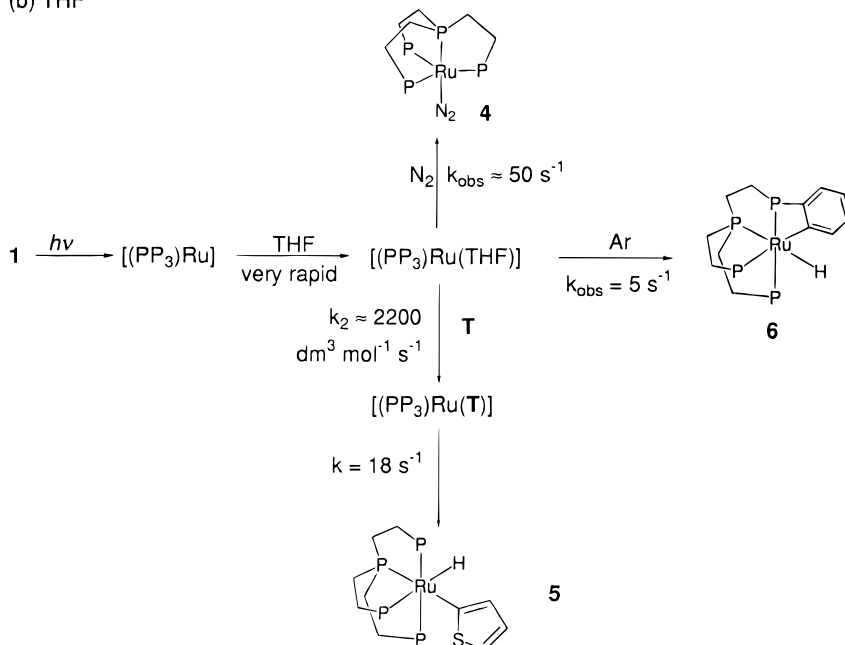
(a) Cyclohexane



$$\text{M} = \text{Ru} \quad \text{k}_2 = (1.4 \pm 0.2) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad \text{k}_{\text{insert}} = 20 \pm 1 \text{ s}^{-1}$$

$$\text{M} = \text{Os} \quad \text{k}_2 = (3.7 \pm 0.1) \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad \text{k}_{\text{insert}} = 8 \pm 1 \text{ s}^{-1}$$

(b) THF



previously observed that rate constants for the reaction of  $[(\text{PP}_3)\text{Ru}]$  show only small variation with substrate.<sup>9</sup> The reactivity of  $[(\text{PP}_3)\text{Os}]$  toward thiophene in cyclohexane is very similar to that of  $[(\text{PP}_3)\text{Ru}]$ , with rate constants for the initial attack and for the insertion step reduced by factors of *ca.* 4 and 2, respectively.

## Discussion

As shown by deuterium labeling experiments,<sup>15</sup> C–H bond cleavage of thiophenes is a reaction occurring on heterogeneous HDS catalysts. Moreover, though there is no evidence which correlates C–H activation to C–S activation under actual reactor conditions, homogeneous modeling studies show that thienyl ligands may be entry points to ring-opening reactions.<sup>16</sup> It is thus surprising that the mechanism of C–H bond cleavage as well as the factors (electronic and steric properties of the metal environment) that control C–H and C–S insertions have not yet been fully elucidated.

It is generally agreed that the C–H bond cleavage of thiophenes by 16-electron metal fragments to give (hydride)thienyl complexes proceeds through the intermediacy of  $\eta^2\text{-C,C}$ -thiophene species,<sup>3,5n</sup> which may be

in equilibrium with  $\eta^1\text{-S}$ -isomers<sup>4n,0</sup> (these are precursors to C–S bond cleavage).<sup>5n,14</sup> The selective formation of C–H insertion products when  $[(\text{PP}_3)\text{Ru}]$  reacts with **T** or 2-CO<sub>2</sub>Et**T** thus suggests the exclusive intermediacy of an  $\eta^2\text{-C,C}$  adduct, although one may not exclude that the two isomers are in equilibrium and that C–S insertion does not occur for steric and electronic reasons (*vide infra*). From the laser flash photolysis experiments, it is not possible to distinguish which intermediate is formed or whether both are present at equilibrium. In fact, the time scale of decay of the **T** adduct is relatively long, so during this period there could be a rapid equilibrium between  $\eta^2\text{-C,C}$  and  $\eta^1\text{-S}$  isomers. From the clean formation of the C–H activation product, one can deduce that the  $\eta^2\text{-C,C}$  adduct must be present. On the other hand, the formation of an  $\eta^1\text{-S}$  complex with Me<sub>2</sub>**T** and the detection of  $[(\text{PP}_3)\text{Ru}(\eta^1\text{-O-THF})]$  (when  $[(\text{PP}_3)\text{Ru}]$  is quenched with only THF)<sup>9</sup> make the initial formation of an S-bound intermediate equally plausible.

In the large majority of thermal reactions between unsaturated metal fragments and thiophenes, C–H insertion is kinetically favored over C–S insertion, but the C–S oxidative-addition products are thermodynamically preferred.<sup>5c,e,h,n,k,o</sup> An exception to the rule is provided by  $[\text{Tp}^*\text{Rh}(\text{PR}_3)]$  ( $\text{Tp}^*$  = hydrotris(3,5-dimethyl-1-pyrazolyl)borate; R = Me, Et), which brings about the activation of both C–H and C–S bonds from **T**, reversing the order of thermodynamic stability.<sup>5a</sup> A

(15) (a) Smith, G. V.; Hickley, C. C.; Behbahany, F. *J. Catal.* **1973**, *30*, 218. (b) Benson, J. W.; Schrader, G. L.; Angelici, R. J. *J. Catal.* **1995**, *96*, 283.

(16) (a) Chisholm, M. H.; Haubrich, S. C.; Martin, J. D.; Streib, W. E. *J. Chem. Soc., Chem. Commun.* **1994**, 683. (b) Erker, G.; Petrenz, R.; Krüger, C.; Lutz, F.; Weiss, A.; Werner, S. *Organometallics* **1992**, *11*, 1646.



particular case is also represented by  $[\text{Cp}_2\text{Mo}]$  and  $[\text{Cp}_2\text{W}]$ , generated by photolysis of dihydride precursors.<sup>5i</sup> The Mo fragment inserts exclusively into an  $\alpha$ -C–H bond of **T** to give a photochemically stable 2-thienyl complex, whereas the W fragment initially forms a C–S insertion product that photochemically converts to the (hydride)2-thienyl isomer by an intramolecular mechanism. Intramolecular mechanisms have also been proposed for the thermal rearrangement of the thienyl and benzo[*b*]thienyl complexes [(triphos)IrH<sub>2</sub>(thienyl)] to the corresponding metallathiacycles,<sup>5e</sup> whereas a dissociative mechanism has been reported for the conversion of the dibenzo[*b,d*]thienyl complex [(triphos)IrH<sub>2</sub>(4-DBTyl)] to the C–S insertion product [(triphos)IrH( $\eta^2$ -C,S-C<sub>12</sub>H<sub>8</sub>S)] (triphos = MeC(CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>).<sup>5c</sup> Finally, irradiation of  $[\text{Fe}(\text{dmpe})_2\text{H}_2]$  at 0 °C in the presence of **T**, 2-methylthiophene, or 3-methylthiophene leads to the formation of both C–H and C–S insertion products (ratio not indicated) which are not photolabile (dmpe = 1,2-bis(dimethylphosphino)ethane).<sup>5j</sup>

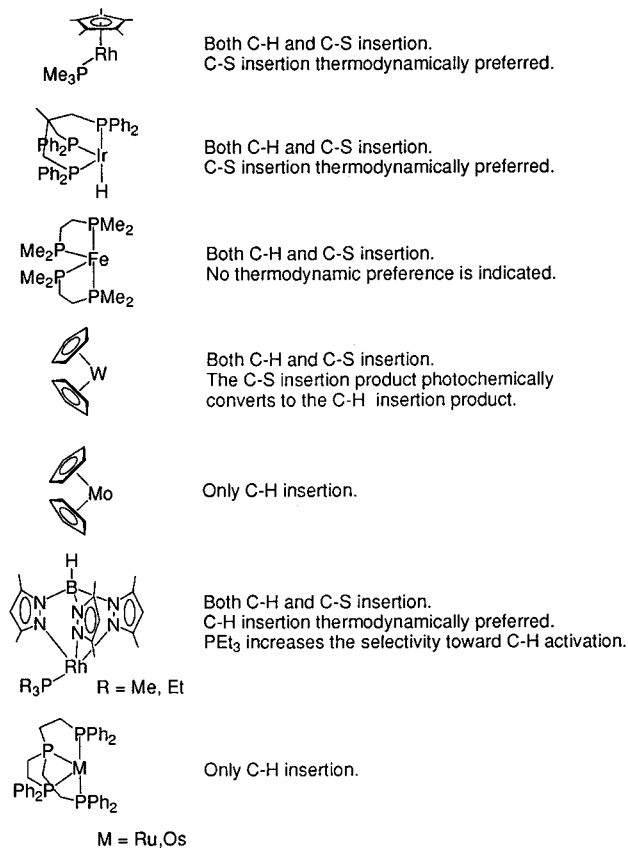
In summary, from a perusal of the metal fragments which are capable of activating C–H bonds in thiophenes (Chart 4), one may infer that C–H insertion is favored by large steric crowding at the metal center while C–S insertion is favored by a high electron density on the metal.

The reactivity of  $[(\text{PP}_3)\text{Ru}]$  toward **T**, 2-CO<sub>2</sub>Et**T**, and 2,5-Me<sub>2</sub>**T** nicely fits this scenario. Among the metal fragments shown in Chart 4,  $[(\text{PP}_3)\text{Ru}]$  is certainly the most encumbered (at least three phenyl substituents point to the incoming thiophene) and one of the least electron-rich together with  $[\text{Cp}_2\text{Mo}]$  and  $[\text{Tp}^*\text{Rh}(\text{PR}_3)]$  which favor C–H activation. Only when the thiophene bears two methyl substituents in the 2,5-positions does  $\eta^1$ -S-coordination prevail over  $\eta^2$ -C,C, but the resulting S-bound adduct does not evolve to the C–S insertion product because the metal slippage from  $\eta^1$ -S to  $\eta^2$ -C,S is hindered by the substituents. In **T** and 2-CO<sub>2</sub>Et**T**, the sulfur atom is a poorer  $\sigma$ -donor and  $\eta^2$ -C,C coordination is thus preferred, leading to selective C–H scission. The ability of the Ru(0) fragment  $[(\text{PP}_3)\text{Ru}]$  to coordinate double bonds has precedent in the synthesis of  $[(\text{PP}_3)\text{Ru}(\text{C}_2\text{H}_4)]$  by treatment of transient  $[(\text{PP}_3)\text{Ru}]$  with ethene.<sup>9</sup>

### Conclusions

The interaction of transient  $[(\text{PP}_3)\text{Ru}]$  with selected thiophenes has been studied. This 16-electron metal fragment reacts with thiophene and ethyl 2-thiophene-carboxylate to give (hydride)2-thienyl complexes, whereas

### Chart 4



an  $\eta^1$ -S complex is formed with 2,5-dimethylthiophene (Schemes 2 and 3). Laser flash photolysis combined with UV–vis detection has shown that an intact Ru(0) thiophene adduct is formed initially, which decays to the C–H activation product with first-order kinetics. The adduct  $[(\text{PP}_3)\text{Ru}(\text{T})]$  is formed from  $\text{Ru}(\text{PP}_3) + \text{T}$  much more rapidly in cyclohexane than in THF. However, the rate constant for conversion of  $[(\text{PP}_3)\text{Ru}(\text{T})]$  to  $[(\text{PP}_3)\text{Ru}(2\text{-Tyl})\text{H}]$  is *ca.* 20 s<sup>-1</sup> in both solvents at 295 K (Chart 3). The selectivity toward C–H insertion exhibited by  $[(\text{PP}_3)\text{Ru}]$  has been interpreted in terms of prevailing steric effects.

**Acknowledgment.** Thanks are due to the Progetto strategico “Tecnologie Chimiche Innovative”, CNR, Rome, Italy, and to the EC (contract ERB IC15CT960746) for financial support. The York group acknowledges the support of EPSRC and British Gas.

OM9703898