

Activation of C–H Bonds in Thiophenes by Rh(PMe₃)₂(CO)Cl: A Low-Temperature NMR Study

Martin G. Partridge, Leslie D. Field,* and Barbara A. Messerle

Department of Organic Chemistry, University of Sydney, Sydney, NSW 2006, Australia

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Irradiation of *trans*-Rh(PMe₃)₂(CO)Cl (**1**) at 230 K in the presence of 2,5-dimethylthiophene or thiophene affords products arising from C–H insertion. Irradiation of **1** in 2,5-dimethylthiophene affords three products: two conformers of the six-coordinate complex *trans*-Rh(PMe₃)₂(CO)(Cl)(2,5-dimethyl-3-thienyl)H, related by rotation about the Rh–C bond, and *trans*-Rh(PMe₃)₂(CO)(2,5-dimethyl-3-thienyl). The major conformer of *trans*-Rh(PMe₃)₂(CO)(Cl)(2,5-dimethyl-3-thienyl)H decays back to **1** at a rate of $(2.9 \pm 0.2) \times 10^{-4} \text{ s}^{-1}$ at 273 K, whereas the minor conformer and *trans*-Rh(PMe₃)₂(CO)(2,5-dimethyl-3-thienyl) are relatively stable. Irradiation of (**1**) in the presence of thiophene affords products arising from addition at both the 2- and 3-positions in the thiophene ring: *trans*-Rh(PMe₃)₂(CO)(Cl)(2-thienyl)H, Rh(PMe₃)₂(CO)(Cl)(3-thienyl)H and *trans*-Rh(PMe₃)₂(CO)(2-thienyl). The six-coordinate Rh(III) species each exist as two rotamers at 230 K related by rotation about the Rh–C_{aryl} bond. Irradiation of **1** in thiophene or 2,5-dimethylthiophene under nitrogen with UV light at low temperatures also gives rise to products arising from thiophene carbonylation.

Introduction

The interaction of thiophenes with transition-metal complexes has been much studied recently as a model for hydrodesulfurization.¹ A number of different reaction and coordination modes for thiophene have been reported in various transition-metal systems,^{2–5} and some of the most studied systems involve organometallic complexes of rhodium and iridium.

Jones and co-workers³ have shown that both C–H and C–S insertion occurs when (C₅Me₅)Rh(PMe₃)(H)₂ is irradiated at low temperature in the presence of thiophene, and the C–H insertion product was identified as (C₅Me₅)Rh(PMe₃)(2-thienyl)H. When the mixture was warmed to room temperature, the C–H insertion product isomerized intramolecularly to the more stable C–S insertion product (C₅Me₅)(PMe₃)RhSCH=CHCH=CH, which was also formed independently by thermolysis of (C₅Me₅)Rh(PMe₃)(C₆H₅)H in thiophene at 60 °C.³ In this system, the independent synthesis of (C₅Me₅)Rh(PMe₃)(3-thienyl)H enabled the

intramolecular isomerization to the more stable 2-thienyl derivative to be studied in detail.

Irradiation of Fe(dmpe)₂(H)₂ in the presence of thiophene or 2-methylthiophene at 273 K generates both the C–H and C–S insertion products.⁶ Recently Jones *et al.*⁷ have shown that irradiation of (C₅H₅)₂Mo(H)₂ in the presence of thiophene generates the C–H insertion product (C₅H₅)₂Mo(2-thienyl)H, whereas irradiation of the corresponding tungsten complex initially yields the C–S insertion product (C₅H₅)₂WSCH=CHCH=CH, which then converts to the C–H insertion product (C₅H₅)₂(2-thienyl)H on further irradiation. The photochemical reactions of Fe(dmpe)₂(H)₂, (C₅Me₅)Rh(PMe₃)(H)₂, and (C₅H₅)M(H)₂ (M = Mo, W) are the only reports (so far) of insertion of a metal into the C–H bonds of thiophenes. Here we report the reactions of *trans*-Rh(PMe₃)₂(CO)Cl (**1**) with thiophene and 2,5-dimethylthiophene, as an extension of our studies on the reaction of **1** with arenes.⁸ The addition products have been characterized using low-temperature NMR techniques.

Results and Discussion

The complex *trans*-Rh(PMe₃)₂(CO)Cl (**1**) has been well-studied with regard to its ability to carbonylate both alkanes and arenes.⁹ We have previously shown that *trans*-Rh(PMe₃)₂(CO)Cl (**1**) when irradiated in benzene/THF at low temperature generates Rh(PMe₃)₂(CO)(Cl)(Ph)H (two isomers) and *trans*-Rh(PMe₃)₂(CO)-Ph, characterized by low-temperature NMR techniques⁸ and independent synthesis.¹⁰

Reaction of *trans*-Rh(PMe₃)₂(CO)Cl (1**) with 2,5-Dimethylthiophene.** A sample of *trans*-Rh(PMe₃)₂-

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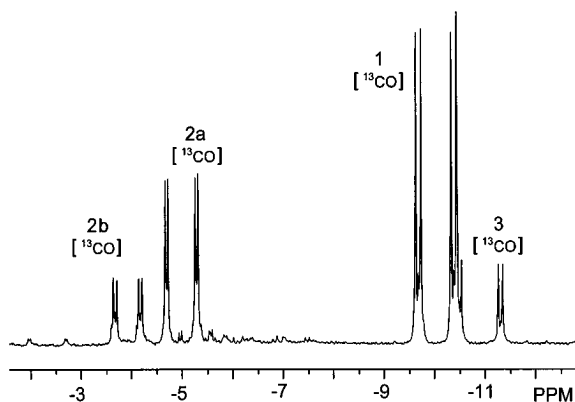
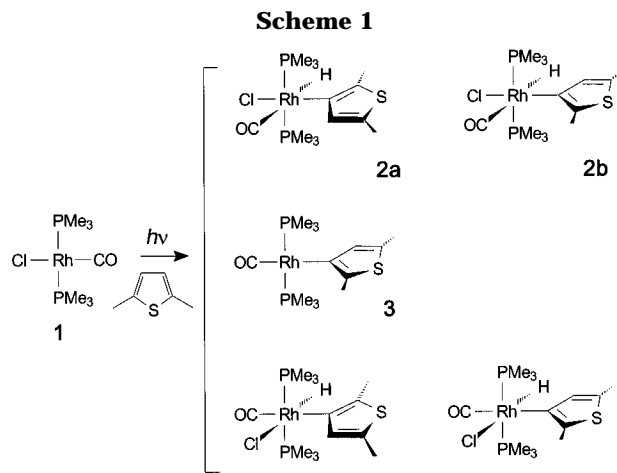


Figure 1. ³¹P NMR spectrum (THF-*d*₈ solvent, 230 K) of the product mixture obtained when Rh(PMe₃)₂(¹³CO)Cl (**1**-¹³CO) was irradiated in the presence of 2,5-dimethylthiophene.

(CO)Cl (**1**; 15 mg in 0.3 mL) was irradiated in a solution of 2,5-dimethylthiophene/THF (1:1) at 230 K. After irradiation, the solvent was removed at low temperature and replaced with THF-*d*₈ for NMR characterization. The ³¹P{¹H} NMR spectrum showed three new products, with rhodium-coupled resonances at δ -5.01 ($^1J_{\text{Rh-P}} = 97.2$ Hz) (**2a**), δ -3.91 ($^1J_{\text{Rh-P}} = 81.2$ Hz) (**2b**), and δ -10.96 ($^1J_{\text{Rh-P}} = 132.2$ Hz) (**3**) in the ratio 0.9:2.0:1.0 after 50% conversion. The high-field region of the ¹H NMR spectrum showed two major metal hydride resonances at δ -7.61 (**2a**) and δ -7.72 ppm (**2b**), with minor hydride resonances (<10% of major hydride products) observed at *ca.* δ -14.0 ppm. All of the metal hydrides exhibit a doublet coupling to ¹⁰³Rh and a triplet coupling to ³¹P. The ¹H resonances of the PMe₃ and 2,5-dimethylthiophene groups in all products were correlated to the resonances in the ³¹P spectrum by ¹H-³¹P COSY spectroscopy.

Complex **1** with ¹³C labeling in the carbonyl group was prepared by stirring **1** under ¹³CO. The ³¹P{¹H} NMR spectrum of the product mixture obtained following irradiation of *trans*-Rh(PMe₃)₂(¹³CO)(Cl) (**1**-¹³CO) in a solution of 2,5-dimethylthiophene/THF (1:1) at 230 K (Figure 1) confirmed the presence of the ¹³CO ligand in all of the photochemically generated products.

In 2,5-dimethylthiophene, there is only one type of aryl C–H bond available for C–H activation. The formation of two major metal hydrides with resonances in the shift range -7.5 to -8 ppm, characteristic of octahedral arylrhodium hydrides with hydride *trans* to carbonyl, Rh(PMe₃)₂(CO)(Cl)(Ar)H,⁸ suggests that Rh(PMe₃)₂(CO)(Cl)(2,5-dimethyl-3-thienyl)H is formed as a mixture of two stable conformers (**2a,b**; Scheme 1). At low temperatures **2a** and **2b** do not interconvert at a significant rate on the NMR time scale. The minor hydride resonances observed near δ -14 ppm are in the



region of the ¹H NMR spectrum characteristic of octahedral arylrhodium hydride complexes of the type Rh(PMe₃)₂(CO)(Cl)(Ar)H with hydride *cis* to carbonyl.⁸

Compound **3** does not contain a hydride ligand, and its ³¹P chemical shift and rhodium–phosphorus coupling constant are similar to those observed in the four-coordinate species *trans*-Rh(PMe₃)₂(CO)(aryl).⁸ The structure **3** is assigned as *trans*-Rh(PMe₃)₂(CO)(2,5-dimethyl-3-thienyl), and its formation can be rationalized by the reductive loss of HCl from the six-coordinate complexes **2a** and/or **2b** in a fashion similar to that reported for the formation of *trans*-Rh(PMe₃)₂(CO)(C₆H₅) from Rh(PMe₃)₂(CO)(Cl)(C₆H₅)H.⁸

When the reaction mixture containing **2a,b** and **3** is warmed to room temperature, **1** is re-formed almost quantitatively. This presumably occurs via reductive elimination of 2,5-dimethylthiophene from the six-coordinate complexes and is analogous to the behavior reported for Rh(PMe₃)₂(CO)(Cl)(Ar)H, where the facile reductive elimination of the arene occurs below room temperature to form Rh(PMe₃)₂(CO)(Cl).⁸ It is not unreasonable that **3** is converted to **1** via an initial reaction with HCl in the reaction mixture to form a six-coordinate complex. If the reaction mixture is taken to dryness at low temperature under high vacuum, *i.e.* under conditions where HCl is removed, **3** is relatively stable at room temperature.

At 230 K there is no evidence for exchange between the conformers **2a** and **2b**. The stereochemistry of these complexes was established by ¹H-¹H NOESY spectroscopy at low temperature (Figure 2). The major product **2a** (with a metal hydride resonance at δ -7.61 ppm) shows strong NOESY cross-peaks correlating the resonance of the metal-bound hydride with the resonance of the PMe₃ ligands at δ 1.50 ppm and also correlating the resonance of the metal-bound hydride with the resonance of one of the thienyl CH₃ groups (at δ 2.39 ppm). There are no NOESY cross-peaks to any of the thienyl protons. In the case of the minor six-coordinate product **2b** (with a hydride resonance at δ -7.72 ppm) there are cross-peaks correlating the resonance of the metal-bound hydride with the resonance of the PMe₃ ligands at δ 1.61 ppm. For **2b**, strong NOESY cross-peaks are also observed between the resonance of the metal-bound hydride and the thienyl proton at δ 7.32 ppm. There are no significant NOESY cross-peaks between the metal hydride and the -CH₃ groups on the thienyl ring (Figure 2).

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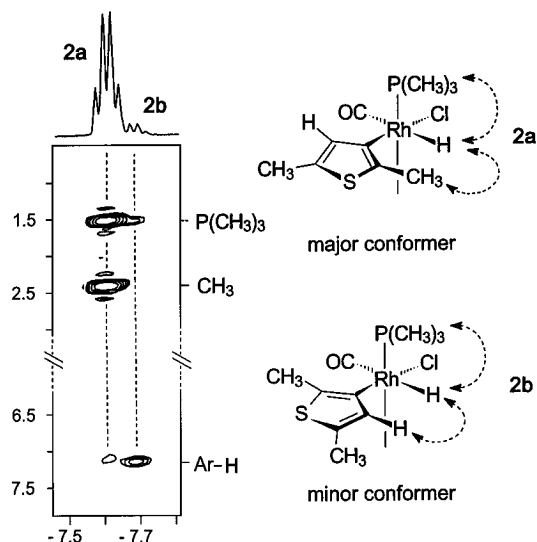
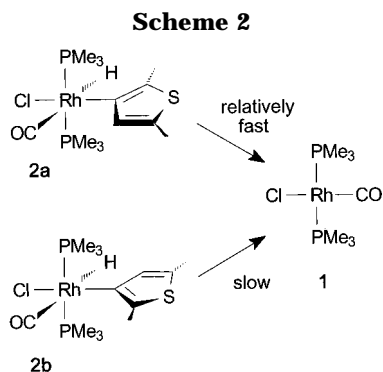


Figure 2. Section of the ^1H - ^1H NOESY spectrum (600 MHz, 230 K, $\text{THF}-d_8$ solvent) of the products **2a** and **2b**, formed following irradiation of $\text{trans-Rh}(\text{PMe}_3)_2(\text{CO})\text{Cl}$ in the presence of 2,5-dimethylthiophene. Only the NOESY cross-peaks involving the metal-bound hydrides are shown.



Kinetics of the Thermal Decomposition of $\text{Rh}(\text{PMe}_3)_2(\text{CO})(\text{Cl})(2,5\text{-dimethyl-3-thienyl})\text{H}$. Irradiation of **1** in 2,5-dimethylthiophene/THF (1:1) at 230 K generates a mixture of **1**, **2a**, **2b**, and **3** in a ratio of approximately 1:1:1:1. The sample was placed in a precooled probe of an NMR spectrometer, and $^{31}\text{P}\{^1\text{H}\}$ spectra were recorded sequentially at regular intervals over a period of time. At 273 K the concentration of **2a** diminished with time in a first-order decay process and the concentration of **1** increased concurrently; the concentration of **2b** and **3** remained constant at this temperature over the period of the experiment. At room temperature, the complexes **2b** and **3** eventually decay to **1** over a period of days. The measured rate at which **2a** decayed to **1** at 273 K was $(2.9 \pm 0.2) \times 10^{-4} \text{ s}^{-1}$, which corresponds to a process with $\Delta G^\ddagger_{273 \text{ K}} = 85.2 \pm 0.2 \text{ kJ mol}^{-1}$.

The fact that the isomer **2a** does not convert to **2b** over the time of the experiment at 273 K indicates that the rate of interconversion of the rotamers is significantly less than the rate of elimination of 2,5-dimethylthiophene from **2a** or **2b** (Scheme 2).

Rotation around the metal-arene bond must be hindered by the presence of a methyl group in the position adjacent to the metalation site. The difference in the thermal stability between **2a** and **2b** with respect to elimination of 2,5-dimethylthiophene must reflect significant stereoelectronic differences between the

isomers, either in their relative thermodynamic stabilities or in their ability to access a transition state from which elimination occurs. In **2b**, the forced proximity of the CO ligand and the bulkier methyl substituents on the thiophene ring may well impede the elimination of the arene compared to the geometry of **2a**, where the corresponding steric interaction (hydrogen to carbonyl) is less.

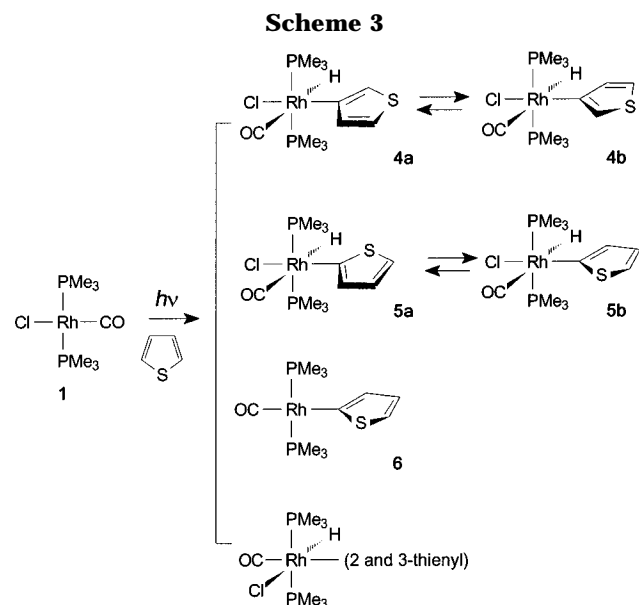
Reaction of $\text{trans-Rh}(\text{PMe}_3)_2(\text{CO})\text{Cl}$ (1**) with Thiophene.** Irradiation of $\text{trans-Rh}(\text{PMe}_3)_2(\text{CO})\text{Cl}$ (**1**; 15 mg) in a 1:1 mixture of thiophene and THF (0.3 mL) at 230 K afforded five major products. The products were characterized using NMR spectroscopy. Following irradiation and removal of the solvent at low temperature under high vacuum, the sample was redissolved in $\text{THF}-d_8$ for NMR characterization. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the product mixture exhibits five new rhodium-coupled resonances at $\delta -5.15$ ($^1J_{\text{Rh-P}} = 96.5 \text{ Hz}$) (**4b**), $\delta -5.33$ ($^1J_{\text{Rh-P}} = 93.4 \text{ Hz}$) (**5b**), $\delta -5.47$ ($^1J_{\text{Rh-P}} = 96.5 \text{ Hz}$) (**4a**), $\delta -6.00$ ($^1J_{\text{Rh-P}} = 94.7 \text{ Hz}$) (**5a**), and $\delta -13.48$ ($^1J_{\text{Rh-P}} = 127.0 \text{ Hz}$) (**6**), in a ratio of 2.9:3.5:3.1:1.0:0.7 after 80% conversion.

In the high-field region of the $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum there were four overlapping hydride resonances (even at 600 MHz) at $\delta -7.61$ ($^1J_{\text{Rh-H}} = 11.8 \text{ Hz}$) (**5b**), $\delta -7.65$ ($^1J_{\text{Rh-H}} = 11.8 \text{ Hz}$) (**4b**), $\delta -7.67$ ($^1J_{\text{Rh-H}} = 12.8 \text{ Hz}$) (**4a**), and $\delta -7.81$ ($^1J_{\text{Rh-H}} = 11.8 \text{ Hz}$) (**5a**). The resonances of all of the metal hydrides show a doublet splitting due to ^{103}Rh and a triplet splitting to ^{31}P . The ^1H chemical shifts of the major metal hydrides (**4a,b**, and **5a,b**) again suggest that these compounds all have the hydride ligands *trans* to a carbonyl group.⁸

In the region of the ^1H NMR spectrum near $\delta -14.0$ there were several hydride resonances which totaled approximately 10% of the intensity of the major hydride resonances near $\delta -7.7 \text{ ppm}$. Again, the minor hydride resonances observed near $\delta -14.0 \text{ ppm}$ are characteristic of six-coordinate arylrhodium compounds with the hydride ligand *cis* to the carbonyl ligand. Irradiation of ^{13}C in the presence of thiophene verified that all five major organometallic products contain a coordinated CO ligand.

Correlation of ^1H and ^{31}P spectra ($^1\text{H}-^{31}\text{P}$ COSY) made it possible to identify and assign the ^{31}P resonances of the metal hydrides. The $^1\text{H}-^{31}\text{P}$ correlation spectrum also shows long-range phosphorus coupling to all of the aromatic protons of the coordinated thienyl rings, and this identified the five unique three-proton spin systems in the aromatic region of the ^1H spectrum. As in the reaction of **1** with 2,5-dimethylthiophene, the ^{31}P resonance at highest field, $\delta -13.48$, does not correlate to a hydride ligand and the chemical shift and the large rhodium-phosphorus coupling constant observed for this species (127 Hz) are similar to those observed in the four-coordinate species $\text{trans-Rh}(\text{PMe}_3)_2(\text{CO})(\text{aryl})$.⁸ Although there would be two positional isomers possible for $\text{trans-Rh}(\text{PMe}_3)_2(\text{CO})(\text{thienyl})$, *i.e.* with substitution at the 2- or 3-positions of the thiophene ring, only one four-coordinate product is observed and this is assigned as the 2-substituted isomer **6** on the basis of the $^1\text{H}-^1\text{H}$ spin spin coupling between the three aromatic protons.

The metal-bound hydride resonances were correlated to the ^{31}P resonances by the use of a $^1\text{H}_{\text{selective}}-^{31}\text{P}$ COSY spectrum which showed that the four resonances in the



³¹P{¹H} NMR spectrum (compounds **4a,b**, and **5a,b**) in the region δ –5 to δ –6 correlate with the four major hydride resonances in the high-field region of the ¹H NMR spectrum.

trans-Rh(PMe₃)₂(CO)Cl (**1**) can add to the C–H bonds of thiophene at either the 2- or 3-positions on the ring, and this gives rise to two positional isomers (**4** and **5**). The presence of four hydride resonances suggests that each of these positional isomers exist as two relatively stable conformers, **4a/4b** and **5a/5b**. Although there is no apparent interconversion between the positional isomers **4** and **5** (on the NMR time scale at 230 K), the ¹H–¹H NOESY spectra are complicated by exchange¹¹ between the conformers, *i.e.* between **4a** and **4b** and between **5a** and **5b** (Scheme 3). The NOESY spectrum in the metal–hydride region shows strong exchange cross-peaks between the metal-bound hydrides of **4a** and **4b** and also between the metal-bound hydrides of **5a** and **5b**.

Complete assignment of the 2- and 3-isomers of the C–H activation products was made using a combination of ¹H–¹H COSY and ¹H–¹H NOESY spectra. When C–H insertion occurs at the 2-position (**5a** and **5b**), H-3 is close in space to the metal-bound hydride in **5a** and a strong NOESY cross-peak was observed correlating the resonance of the hydride at –7.61 ppm with the resonance of the thienyl proton at 6.49 ppm. C–H insertion at the 3-position (**4a** and **4b**) allows H-2 of the thienyl ring to be close in space to the rhodium hydride in **4a** and H-4 in **4b**, and the two hydride resonances at –7.65 and –7.67 ppm exhibit strong NOESY cross-peaks with the aromatic resonances at 6.82 and 6.54 ppm, respectively. The assignment of the remaining resonances follows.

A summary of NMR data for compounds **2a,b**, **3**, **4a,b**, **5a,b**, and **6** is given in Table 1.

Magnitudes and Signs of Heteronuclear Coupling Constants. Irradiation of **1**-¹³CO in 2,5-dimethylthiophene generates **2a**-¹³CO and **2b**-¹³CO. The

relative signs of the couplings ²J¹³C–Rh–H, ²J¹³C–Rh–P, and ²J_{P–Rh–H} in **2a**-¹³CO and **2b**-¹³CO were measured using selective two-dimensional ¹H–X correlation experiments.^{12ab} The signs of ²J¹³C–Rh–H, ²J¹³C–Rh–P and ²J_{P–Rh–H} are the same as those previously measured for Rh(PMe₃)₂(CO)(Cl)(C₆H₅)H, where the ¹³CO ligand and the hydride are *trans* to one another (Table 2).^{12b} The magnitudes of all heteronuclear coupling constants are also of magnitude similar to those observed for Rh(PMe₃)₂(CO)(Cl)(C₆H₅)H. This supports the assignment of the stereochemistry about the metal center described above for **2a** and **2b**. The heteronuclear coupling constants determined for **2a** and **2b** add to the expanding set of coupling constants which have now been measured in organometallic complexes, and these can be used to establish the stereochemistry of related complexes.^{12b}

Carbonylation Products. After irradiation of **1** in 2,5-dimethylthiophene or thiophene, the low-field region of the ¹H NMR spectrum showed the presence of aldehyde resonances at *ca.* 9.9 ppm. Following irradiation of **1**-¹³CO in 2,5-dimethylthiophene, the low-field region of the ¹H NMR spectrum showed a ¹³C-coupled doublet at δ 10.03 (²J_{C–H} = 173 Hz), confirming the formation of aldehyde products in the reaction mixture.¹³ GCMS analysis of the reaction mixture following irradiation of 2,5-dimethylthiophene with **1** confirmed the formation of 2,5-dimethylthiophene-3-carboxaldehyde as well as (2,5-dimethyl-3-thienyl) ketone and 2,2',5,5'-tetramethyl-3,3'-bithienyl (Scheme 4). Although the reactions of thiophenes with **1** under conditions which could give rise to higher yields of carbonylated products (*i.e.* reaction under a carbon monoxide atmosphere) have not yet been investigated, there are clear indications that *trans*-Rh(PMe₃)₂(CO)Cl may serve as a carbonylation or coupling catalyst for thiophenes in a fashion similar to its reaction with aromatic substrates.⁸

Summary and Conclusions

Irradiation of *trans*-Rh(PMe₃)₂(CO)Cl (**1**) at 230 K in the presence of thiophene and 2,5-dimethylthiophene affords a number of six-coordinate C–H insertion products with no evidence for insertion into the C–S bond or breakdown of the aromatic ring. Irradiation of **1** in 2,5-dimethylthiophene yields three products, including the six-coordinate complex Rh(PMe₃)₂(CO)(Cl)-(2,5-dimethyl-3-thienyl)H as two rotamers. Thermally, the major product **2a** decays back to **1** more rapidly than does the minor isomer **2b**, and the difference in decomposition rates may be attributed to stereoelectronic effects.

In the case of thiophene, **1** inserts into the C–H bonds at both the 2- and 3- positions in the aryl ring to yield the six-coordinate complexes Rh(PMe₃)₂(CO)(Cl)(2-thienyl)H and Rh(PMe₃)₂(CO)(Cl)(3-thienyl)H.

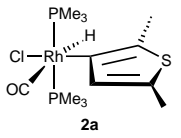
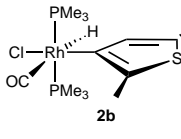
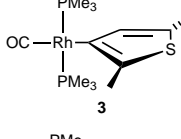
All of the six-coordinate rhodium thienyl compounds exhibit restricted rotation on the NMR time scale about the thienyl–Rh bond. The four-coordinate Rh(I) complexes *trans*-Rh(PMe₃)₂(CO)(2,5-dimethyl-3-thienyl) and *trans*-Rh(PMe₃)₂(CO)(thienyl) are also formed on ir-

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Table 1. NMR Data for Complexes 2–7 Recorded at 230 K

complex		δ /ppm (J/Hz)	assign
 2a	$^1\text{H NMR}$	6.41 (s) 2.42 (s) 2.39 (s) 1.50 (vt, spacing 3.4) -7.61 (dtd, $^2J_{\text{C}^3\text{H}} = -67$, $^2J_{\text{PH}} = 15$, $^1J_{\text{RhH}} = 12$) -5.01 (dd, $^1J_{\text{RhP}} = 97.2$, $^2J_{\text{C}^3\text{P}} = 8.6$)	H-4 CH ₃ CH ₃ PMe ₃ Rh-H PMe ₃
	$^{31}\text{P}\{^1\text{H}\}$ NMR		
	$^1\text{H NMR}$	7.32 (s) 2.47 (s) 2.42 (s) 1.61 (vt, spacing = 3.7) -7.72 (dtd, $^2J_{\text{C}^3\text{H}} = -68$, $^2J_{\text{PH}} = 14$, $^1J_{\text{RhH}} = 12$) -3.91 (dd, $^1J_{\text{RhP}} = 81.2$, $^2J_{\text{C}^3\text{P}} = 11.1$)	H-4 CH ₃ CH ₃ PMe ₃ Rh-H PMe ₃
	$^{31}\text{P}\{^1\text{H}\}$ NMR		
	$^1\text{H NMR}$	6.24 (s) 2.45 (s) 2.41 (s) 1.36 (vt, spacing 3.4) -10.96 (dd, $^1J_{\text{RhP}} = 132.2$, $^2J_{\text{C}^3\text{P}} = 13.6$)	H-4 CH ₃ CH ₃ PMe ₃ PMe ₃
 2b	$^1\text{H NMR}$	7.25 (dd) 6.82 (m) 6.56 (m) 1.45 (vt, spacing 3.2) -7.67 (d, $^1J_{\text{RhH}} = 12.8$) -5.47 (d, $^1J_{\text{RhP}} = 96.5$)	H-5 H-4 H-2 PMe ₃ Rh-H PMe ₃
	$^{31}\text{P}\{^1\text{H}\}$ NMR		
	$^1\text{H NMR}$	7.29 (dd) 6.82 (m) 6.56 (m) 1.45 (vt, spacing 3.2) -7.65 (d, $^1J_{\text{RhH}} = 11.8$) -5.15 (d, $^1J_{\text{RhP}} = 96.5$)	H-5 H-4 H-2 PMe ₃ Rh-H PMe ₃
	$^{31}\text{P}\{^1\text{H}\}$ NMR		
	$^1\text{H NMR}$	7.22 (d) 6.85 (dd) 6.49 (d) 1.48 (vt, spacing 3.5) -7.81 (d, $^1J_{\text{RhH}} = 11.8$) -6.00 (d, $^1J_{\text{RhP}} = 94.7$)	H-5 H-4 H-3 PMe ₃ Rh-H PMe ₃
 3	$^1\text{H NMR}$	7.26 (d) 6.87 (dd) 6.50 (d) 1.48 (vt, spacing 3.5) -7.61 (d, $^1J_{\text{RhH}} = 11.8$) -5.33 (d, $^1J_{\text{RhP}} = 93.4$)	H-5 H-4 H-3 PMe ₃ Rh-H PMe ₃
	$^{31}\text{P}\{^1\text{H}\}$ NMR		
	$^1\text{H NMR}$	7.49 (d, $J = 4.9$) 7.07 (dd) 6.62 (d, $J = 2.9$) 1.32 (vt, spacing 3.1) -13.48 (d, $^1J_{\text{RhP}} = 127.0$)	H-5 H-4 H-3 PMe ₃ PMe ₃
	$^{31}\text{P}\{^1\text{H}\}$ NMR		
	$^1\text{H NMR}$		

^a Legend: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, vt = virtual triplet.

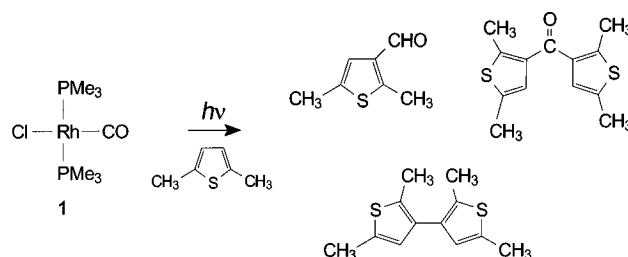
Table 2. Summary of Significant Core Heteronuclear Coupling Constants^a for 2a and 2b

J -Coupling	2a	2b
$^2J_{\text{C}^3\text{-M-H}}$	-67	-68
$^2J_{\text{P-M-H}}$	15	14
$^2J_{\text{C}^3\text{-M-P}}$	8.6	11.1

^a Coupling constants in Hz.^{12b}

radiation of **1** in 2,5-dimethylthiophene and thiophene, respectively. These complexes arise from initial reaction of **1** with the thiophene followed by reductive loss of HCl.

Irradiation of **1** in thiophene or 2,5-dimethylthiophene at low temperatures brings about thiophene coupling and carbonylation. The products formed are analogous

Scheme 4

to those formed on irradiation of **1** in the presence of benzene and other aromatic compounds.

Experimental Section

General Information. All operations were performed under a nitrogen atmosphere, either on a vacuum line using standard Schlenk methods or in a drybox. Rhodium trichloride was obtained as a generous loan from Johnson Matthey PLC.

Trimethylphosphine was obtained from Aldrich Chemicals and used without further purification. Nitrogen (>99.5%) and carbon monoxide (>99.5%) were purchased from CIG-HYTEC. ^{13}C O (99 atom % ^{13}C , 10.5% ^{18}O) was purchased from Isotec Inc. Gases were used without further purification. THF was distilled under an atmosphere of nitrogen from purple solutions of sodium benzophenone ketyl.

NMR spectra were recorded on Bruker AMX400 (1H NMR at 400.13 MHz, ^{31}P NMR at 162.0 MHz, and ^{13}C NMR at 100.6 MHz) and AMX600 (1H at 600.13 MHz) spectrometers. The probe temperature of the NMR spectrometers was regulated by a Bruker BVT 2000 temperature controller and calibrated against the proton spectrum of methanol.¹⁴ Deuterated THF- d_8 was obtained from Merck and was distilled under an atmosphere of nitrogen from purple solutions of sodium benzophenone ketyl prior to use. NMR samples for study were prepared in 5 mm NMR tubes fitted with concentric Youngs PTFE valves.¹⁵ Low-temperature irradiations were carried out using a 125 W medium-pressure mercury vapor lamp with the sample tube suspended in a double-walled Pyrex Dewar containing ethanol cooled with a refrigeration coil.

NMR Spectroscopy. All samples for NMR characterization had THF and the thiophene removed under high vacuum at low temperature (230 K), and THF- d_8 was added for recording NMR data. NMR data processing was done using Sun Sparc station processing facilities with standard Bruker software. In the presentation of NMR data, chemical shifts (δ) are in ppm, the downfield region being positive. 1H and ^{13}C chemical shifts are referenced to residual solvent resonances. ^{31}P chemical shifts are referenced to external, neat trimethyl phosphite, taken as 140.85 ppm at the temperature quoted. Broad-band decoupling of one- and two-dimensional ^{13}C and ^{31}P spectra was achieved with composite pulse 1H decoupling using the WALTZ-16 sequence.¹⁶ Heteronuclear decoupling of one- and two-dimensional 1H and heteronuclear spectra was achieved with composite pulse decoupling using

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the GARP sequence¹⁷ during the acquisition only. All homonuclear two-dimensional 1H spectra were acquired using ^{31}P decoupling in both dimensions. All homonuclear and heteronuclear two-dimensional NMR experiments were acquired using TPPI.¹⁸ 2D COSY and NOESY spectra were typically acquired with 512 increments of 16 transients. Cosine weighting was used prior to Fourier transformation. The mixing interval for 2D-NOESY experiments was 1.6 s. Base line distortions were removed using a polynomial fit of order 3 for 2D-NOESY spectra. 1H -detected, selective H–X correlation experiments used a “top hat” pulse shape for excitation¹⁹ with shaped pulses defined by 256 steps. A pulse length of 15 ms was calibrated to have an effective 1H excitation window of ca. 250 Hz. Selective, inverse detection H–X correlation experiments were acquired with 256 increments of 16 transients.

Syntheses. The preparations of *trans*- $Rh(PMe_3)_2(CO)Cl$ (**1**)²⁰ and **1- ^{13}C** ⁸ have been reported previously.

Kinetic Analyses. The decomposition of **2a** was followed quantitatively by ^{31}P NMR spectroscopy. Spectra (16 scans, total acquisition time for each spectrum 1.2 min) were accumulated automatically at intervals in a spectrometer whose probe temperature had been stabilized. Spectra were automatically integrated and data fitted to an exponential decay **3** \rightarrow **1**, using a nonlinear regression analysis.

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