# Acid-Promoted Rearrangement of the Metalated Thienyl Rings in Dirhodium(II) Complexes with Thienyl Phosphines as Ligands[⊥]

Julio Lloret,[†] Francisco Estevan,[†] Pascual Lahuerta,*[,†] Pipsa Hirva,[‡]
Julia Pérez-Prieto,*[,§] and Mercedes Sanaú[†]

*Departamento de Química Inorgánica, Facultad de Química, Universidad de Valencia, Dr. Moliner 50, 46100 Burjassot, Valencia, Spain, Department of Chemistry, University of Joensuu, P.O. Box 111, FIN-80101 Joensuu, Finland, and Departamento de Química Orgánica/Instituto de Ciencia Molecular, Universidad de Valencia, Polígono La Coma s/n, 46980 Paterna, Valencia, Spain*

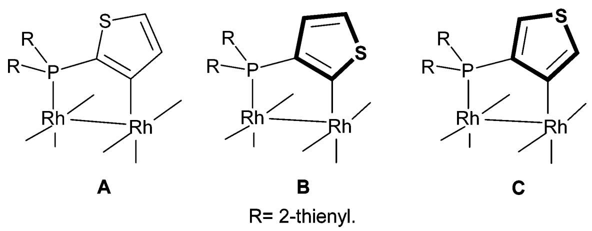
*Received February 21, 2006*

Several mono- and bis-cyclometalated compounds have been prepared and characterized from the thermal reaction of dirhodium(II) tetraacetate and tris(2-thienyl)phosphine, $P(2\text{-}C_4H_3S)_3$ (**1**), in toluene/acetic acid mixtures. In refluxing acetic acid, the mono-cyclometalated compound $Rh_2(O_2CCH_3)_3[(2\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2](CH_3CO_2H)_2$ (**2A**) isomerizes to $Rh_2(O_2CCH_3)_3[(3\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2](CH_3CO_2H)_2$ (**2B**), which results from the selective rearrangement of the metalated ring from a 2-thienyl to a 3-thienyl structure. In the same conditions, the bis-cyclometalated compounds of formula $Rh_2(O_2CCH_3)_2[(2\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2]_2(CH_3CO_2H)_2$ and with head-to-tail (**3AA**) or head-to-head (**4AA**) configuration of the phosphines undergo similar rearrangement, yielding compounds $Rh_2(O_2CCH_3)_2[(3\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2]_2(CH_3CO_2H)_2$, **3BB** and **4BB**, respectively. Compounds with only one ring of the thienyl phosphine rearranged, $Rh_2(O_2CCH_3)_2[(3\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2][(2\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2](CH_3CO_2H)_2$, **3AB** and **4AB**, have also been isolated. The fastest rearrangement occurs in **2A** and the slowest in **3AA**. Isotopic labeling experiments show that the rearrangement of the metalated rings in compounds **2A**, **3AA**, and **4AA** and the electrophilic Rh−C bond cleavage occur with different rates, indicating that they are independent processes. All the synthesized compounds have been structurally characterized by multinuclear NMR spectroscopy, and some representative compounds were also analyzed by X-ray methods. The free ligand **1** does not experience isomerization under the conditions that metalated phosphines do. DFT calculations confirm that the observed rearrangement is driven by enthalpy.

## Introduction

Cyclometalation of aryl phosphines is a well-known and often used reaction for the preparation of organometallic compounds.[1−3] The first dirhodium (II) compound of this type, *cis*-$Rh_2(O_2CCH_3)_2[(C_6H_4)PPh_2)_2](CH_3CO_2H)_2$, was reported by Cotton et al. in 1985.[4] Later on, many compounds of the general formula $Rh_2(PC)_2(O_2CR)_2$, PC representing a metalated aryl phosphine, have been prepared by direct thermal reaction of the corresponding phosphine with dirhodium(II) tetracarboxylate.[5,6] These compounds show activity and chemoselectivity in the catalytic transformation of α-diazocarbonyl compounds.[7] These compounds with head-to-tail arrangement of the metalated phosphines are inherently chiral. The use of enantiomerically pure compounds has been exploited for enantioselective reactions.[8−11]

**Scheme 1. Schematic Drawing of the Thienyl Ring Arrangement**



We were interested in preparing a new family of metalated dirhodium(II) compounds with thienyl phosphines, to test the influence of these heteroaromatic rings in the catalytic behavior of the new compounds. In a previous communication, we have reported that a rearranged compound was obtained by serendipity in the workup of the reaction of dirhodium(II) tetraacetate with tris(2-thienyl)phosphine (**1**).[12] Such rearrangement, from structure **A** to **B** (Scheme 1), affected only the metalated rings, while the remaining substituents retained their original structure.

---

[⊥] Dedicated to Dr. J. Antonio Abad on the occasion of his retirement, with best wishes.

* To whom correspondence should be addressed. P.L.: Fax: (34)-963544322. E-mail: pascual.lahuerta@uv.es. J.P.: Fax: (34)963543274. E-mail: julia.perez@uv.es.

[†] Departamento de Química Inorgánica, Universidad de Valencia.

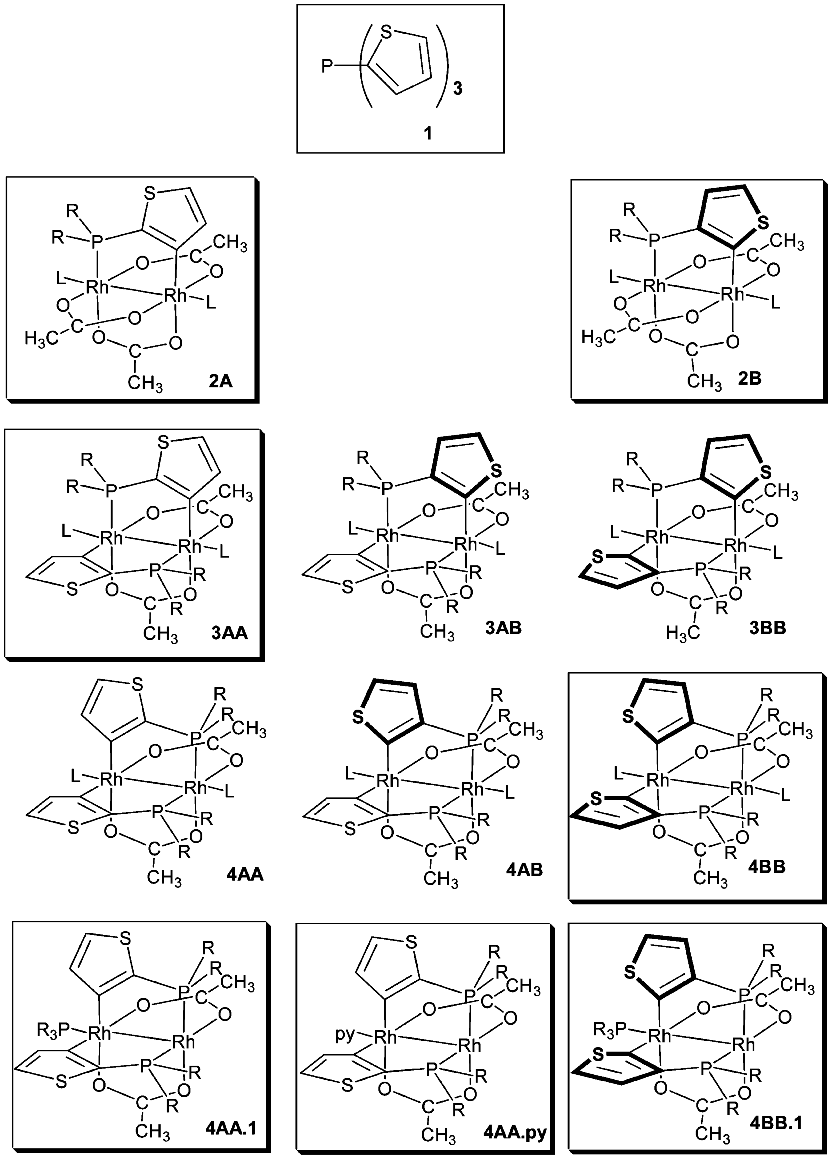
[‡] University of Joensuu.

[§] Departamento de Química Orgánica/Instituto de Ciencia Molecular, Universidad de Valencia.

(1) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403.
(2) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879.
(3) Van der Moom, M.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759.
(4) Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A.; Tocher, J. H. *Organometallics* **1985**, *4*, 8.
(5) Morrison, E. C.; Tocher, D. A. *Inorg. Chim. Acta* **1989**, *156*, 99.
(6) Lahuerta, P.; Payá, J.; Pellinghelli, M. A.; Tiripicchio, A. *Inorg. Chem.* **1992**, *31*, 1224.
(7) Estevan, F.; Lahuerta, P.; Pérez-Prieto, J.; Sanaú, M.; Stiriba, S. E.; Úbeda, M. A. *Organometallics* **1997**, *16*, 880.
(8) Taber, D. F.; Malcolm, S. C.; Bieger, K.; Lahuerta, P.; Sanaú, M.; Stiriba, S. E.; Pérez-Prieto, J.; Monge, M. A. *J. Am. Chem. Soc.* **1999**, *121*, 860.
(9) Estevan, F.; Herbst, K.; Lahuerta, P.; Barberis, M.; Pérez-Prieto, J. *Organometallics* **2001**, *20*, 950.
(10) Barberis, M.; Lahuerta, P.; Pérez-Prieto, J.; Sanaú, M. *J. Chem. Soc., Chem. Commun.* **2001**, 439.
(11) Barberis, M.; Pérez-Prieto, J.; Herbst, K.; Lahuerta, P. *Organometallics* **2002**, *21*, 1667.
(12) Bieger, K.; Estevan, F.; Lahuerta, P.; Lloret, J.; Perez-Prieto, J.; Sanaú, M.; Siguero, N.; Stiriba, S. E. *Organometallics* **2003**, *22*, 1799.

10.1021/om0601697 CCC: $33.50

**Scheme 2. Mono- and Bis-cyclometalated Compounds Obtained from Phosphine 1**



R = 2-thienyl; L = $CH_3CO_2H$

Herein, we wish to report our results in full, including additional experiments and theoretical studies performed to gain a deeper insight into this unusual rearrangement. The synthesis and characterization of three cyclometalated dirhodium(II) compounds, $Rh_2(O_2CCH_3)_3[(2\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2](CH_3CO_2H)_2$ (**2A**), (H−T)$Rh_2(O_2CCH_3)_2[(2\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2]_2(CH_3CO_2H)_2$ (**3AA**), and (H−H)$Rh_2(O_2CCH_3)_2[(2\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2]_2(CH_3CO_2H)_2$ (**4AA**), is described. The preparation and structural characterization of new cyclometalated compounds with the metalated thienyl rings having structure **B** is also described (Scheme 2). The numbering scheme used includes one or two letters that refer to the structure of the metalated ring(s) in mono- and bis-cyclometalated compounds, respectively. Some mechanistic information is obtained by reacting the compounds in deuterated acetic acid. The relative energies of all the compounds were established by DFT calculations.

## Results and Discussion

**Reactions of Rhodium Tetraacetate and Tris(2-thienyl)phosphine (1). Synthesis of Compounds 2A, 3AA, and 4AA.** The thermal reaction of dirhodium(II) tetraacetate and **1** (1:0.8 molar ratio) for 2 h in refluxing (9:1) toluene/acetic acid produced the mono-cyclometalated compound $Rh_2(O_2CCH_3)_3[(2\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2](CH_3CO_2H)_2$ (**2A**) as the main product, which was isolated in 60% yield (Scheme 2). The bis-cyclometalated compounds (H−T)$Rh_2(O_2CCH_3)_2[(2\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2]_2(CH_3CO_2H)_2$ (**3AA**) and (H−H)$Rh_2(O_2CCH_3)_2[(2\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2]_2(CH_3CO_2H)_2$ (**4AA**), also present in solution (ca. 10% each), were prepared in better yields by reaction of dirhodium(II) tetraacetate and **1** (1:2.15 molar ratio) in toluene/acetic acid mixtures of different composition. The reaction time was an important variable, as evolution of **4AA** to **3AA** was observed after extended heating in a 9:1 toluene/acetic acid mixture (see Figure S5 and Table S1 in the Supporting Information). All the efforts to selectively produce only one of these two products by thermal reactions were unsuccessful. The relative amount in which these two compounds were prepared depended also on the amount of acid used in the reaction. The best yield of **4AA**, 75%, was obtained using a 2:1 toluene/acetic acid mixture as reaction solvent.

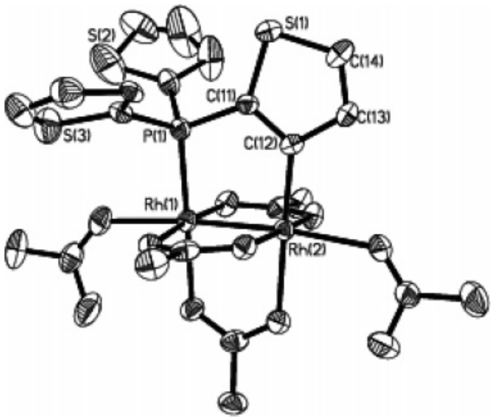


**Figure 1.** ORTEP view of compound **2A** with ellipsoids representing 30% probability and H atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Rh(1)−Rh(2), 2.4385(8); Rh(1)−P(1), 2.204(2); Rh(2)−C(12), 1.957(7); P(1)−Rh(1)−Rh(2), 92.32(5); Rh(1)−Rh(2)−C(12), 94.53(18).

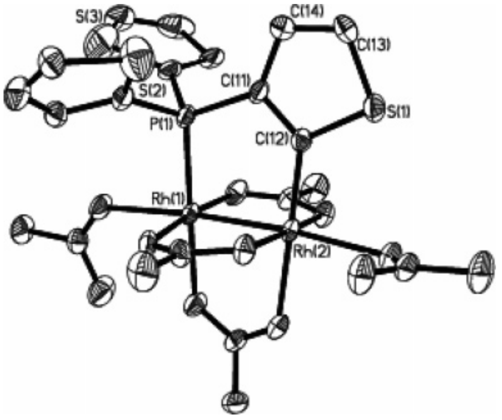


**Figure 2.** ORTEP view of compound **2B** with ellipsoids representing 30% probability and H atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Rh(1)−Rh(2), 2.4341(7); Rh(1)−P(1), 2.206(2); Rh(2)−C(12), 1.971(7); P(1)−Rh(1)−Rh(2), 92.86(5); Rh(1)−Rh(2)−C(12), 92.9(2).

Irradiation (mercury lamp, Pyrex filter, 2.5 h) of a solution of dirhodium(II) tetraacetate and **1** ($Rh_2$:**1** ratios from 1:1 to 1:2) in a 9:1 $CH_2Cl_2$/acetic acid mixture led only to **3AA**, which was isolated in high yield. Alternatively, short irradiation (15 min) of a mixture of the mono-cyclometalated compound **2A** and **1** produced **3AA**. This rapid photoinduced metalation has no precedent in related studies with triarylphosphines.[13,14]

All the isolated compounds were characterized by multinuclear NMR spectroscopy. The molecular structure of compounds **2A** (Figure 1) and **3AA** (Figure S9 in SI), as adducts with two molecules of acetic acid, were obtained by X-ray methods. Compound **4AA** was characterized by NMR spectroscopy (see Figure S4a in SI), but all the attempts to obtain single crystals of **4AA** failed. However, it was crystallized as an adduct with pyridine or tris(2-thienyl)phosphine (**4AA·py** and **4AA·1**) (see Figures S10 and S11 in SI). In both structures, the two cyclometalated phosphines were in a head-to-head (H−H) disposition, and the axial pyridine or phosphine ligands coordinate the less sterically hindered rhodium atom in the binuclear unit, namely, the one having a $RhO_2C_2$ environment.

**Synthesis of 2B.** The chemical evolution of **2A** in refluxing acetic acid was easily monitored by $^{31}P$ NMR spectroscopy, following the disappearance of the signal at 0.6 ppm (due to **2A**) and the appearance of a new signal at −3.0 ppm (due to **2B**) (see Figure S6 in SI). No other species were observed in solution. The transformation was completed after 20 h; $Rh_2(O_2CCH_3)_3[(3\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2](CH_3CO_2H)_2$ (**2B**) was isolated in high yield. 2D NMR experiments (Figure S2 in SI), as well as X-ray crystal structure determination (Figure 2), support the structure assignment for **2B** (Scheme 2).

**Synthesis of 3AB and 3BB.** Compound **3AA** was heated in refluxing acetic acid for 18 h. The $^{31}P$ NMR spectrum of the reaction mixture confirmed the presence of two new products. One, $Rh_2(O_2CCH_3)_2[(2\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2][(3\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2](CH_3CO_2H)_2$ (**3AB**), resulted from the rearrangement of one metalated ring, while the second product, $Rh_2(O_2CCH_3)_2[(3\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2]_2(CH_3CO_2H)_2$ (**3BB**), contained both metalated rings rearranged (Scheme 2 and Figure S7 and Table S2 in SI). The spectroscopic yields prior to isolation were 25% (**3AA**), 48% (**3AB**), and 12% (**3BB**). Signals belonging to phosphine oxide and **2B** were also detected in the spectrum in smaller amounts. From this reaction mixtures, **3AB** was isolated with moderate yields and spectroscopically characterized. Longer heating (>150 h) increased the relative amount of **3BB**, though simultaneously decomposition was observed. From this reaction mixture, **3BB** was isolated in a 30% yield and spectroscopically characterized.

Alternatively, these two compounds, **3AB** and **3BB**, were obtained in 20−30% yield from the reaction of dirhodium(II) tetraacetate with **1** (1:2 molar ratio) in pure acetic acid.

Two experimental observations support that **3AB** is the intermediate in the transformation of **3AA** to **3BB**. Thus, **3AB** shows two different phosphorus environments in the $^{31}P$ NMR spectra, while both **3AA** and **3BB** exhibit single phosphorus environments. Also, the relative intensities of the signals due to the three compounds **3AA**, **3AB**, and **3BB** were time-dependent and fully agreed with an evolution from **3AA** to **3AB** to **3BB**. Besides, **3AB** was the only spectroscopically detected product when **2B** reacted with **1** in the above-described photochemical conditions.

2D NMR experiments on **3BB** confirmed the structural assignment for this compound (see Figure S3 in SI).

**Synthesis of 4AB and 4BB.** We have observed that, in acetic acid, **4AA** undergoes rearrangement of the metalated rings much faster than **3AA**. Taking advantage of this observation, we heated a 1:3 mixture of **3AA** and **4AA** in acetic acid at 105 °C. A new species, identified as $Rh_2(O_2CCH_3)_2[(2\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2][(3\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2](CH_3CO_2H)_2$ (**4AB**), was formed with simultaneous disappearance of **4AA** (Figure S8 and Table S3 in SI). After 10 h of heating, **4AB** was present in solution in a 50% spectroscopic yield, though after the chromatographic isolation only 30% of the product was obtained. During this time the amount of **3AA** in solution remained unchanged.

Extended heating produced the appearance of a new species, $Rh_2(O_2CCH_3)_2[(3\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2]_2(CH_3CO_2H)_2$ (**4BB**), that finally became the major product in solution. However, this reaction yielded **4BB** only in moderate yield due to extensive decomposition. Alternatively, compound **4BB** was best prepared by direct reaction of dirhodium(II) tetraacetate and **1** in refluxing acetic acid.

Multinuclear NMR studies confirmed the structural characterization made for these two compounds (see Figure S4b in SI for **4BB**). All the efforts to obtained single crystals of **4AB** failed. Compound **4BB** had been previously characterized by X-ray methods.[12] **4AB** and **4BB** form adducts with tris(2-

---

(13) González, G.; Martinez, M.; Estevan, F.; García-Bernabé, A.; Lahuerta, P.; Peris, E.; Úbeda, M. A.; Díaz, R.; García-Granda, S.; Tejerina, B. *New J. Chem.* **1996**, *20*, 83.

(14) Alarcón, C. J.; Lahuerta, P.; Peris, E.; Úbeda, M. A.; Aguirre, A.; García-Granda, S.; Gómez-Beltrán, F. *Inorg. Chim. Acta* **1997**, *254*, 177.

thienyl)phosphine, **4AB·1** and **4BB·1**. Some crystallographic results related to these adducts were obtained (see later).

**Structural Characterization. Structures of Compounds 2A and 2B.** These compounds crystallize in the monoclinic system, space groups *P*2(1)*/n* and *P*2(1), respectively. Both structures are depicted in Figures 1 and 2, together with selected bond distances and bond angles. Each compound is composed of one dirhodium unit that contains one cyclometalated [$(C_4H_2S)P(2\text{-}C_4H_3S)_2$] ligand and three carboxylate groups. The two identical axial ligands are identified as acetic acid molecules.

The Rh−Rh bond distances of 2.4385(8) and 2.4341(7) Å for **2A** and **2B**, respectively, are similar to those found in other monometalated dirhodium complexes with a rhodium−rhodium bond.[6] The Rh−P, Rh−C, and Rh−O distances are also within the expected range of values for this type of compound.[6] In each compound, the Rh−O bond distance *trans* to C [2.192(5) Å in **2A** and 2.172(6) Å in **2B**] is slightly longer than that *trans* to P [2.154(5) Å in **2A** and 2.142(6) Å in **2B**], and both are also longer than the remaining four Rh−O bond distances *trans* to O (average value 2.04 Å). The Rh−C bond distance in compounds **2A** and **2B** [1.957(7) Å in **2A** and 1.971(7) Å in **2B**] is slightly shorter than the values observed for the compound with triphenylphosphine [1.999(5) Å].[4] All the remaining structural parameters are very similar, and the differences are not significant.

The metalated thienyl rings are essentially planar. The location of the sulfur atom, unambiguously defined in each case and in complete agreement with the 2D NMR results (see later), was the main structural difference between these two compounds. In **2A** the sulfur atom is close to the carbon atom attached to phosphorus (structure type **A**), while in **2B** it is close to the carbon atom attached to rhodium (structure type **B**). The rings are not regular due to the C−S bond distances (average value 1.71 Å), which are much longer than the C−C bond distances, which follow the short−long−short trend expected for a diene system (average values of 1.36−1.45−1.37 Å). Some disorder was observed in **2A**, due to the existence of two different orientations in the nonmetalated rings, related by a 180° rotation around the P−C bond. As that information was not relevant, the structure was refined locating the sulfur atom in the position that gave the best refinement. As usual, the axial acetic acid molecules have the OH group oriented toward an oxygen atom of one of the bridging carboxylate ligands. However, while in **2A** both OH groups are interacting with the carboxylate *trans* to the metalated phosphine, in **2B** the two OH groups interact with two carboxylate groups that are mutually *cis*.

The metalated phosphine is significantly less twisted than in the analogous mono-metalated compounds with triaryl phosphines. Thus, the P−Rh−Rh−C torsion angles for **2A** and **2B** are in the range 6.3−7.2°, while the reported values for the compounds with triaryl phosphines are in the range 11.1−18.9°.

**Structures of Bis-cyclometalated Compounds.** The main structural features described for the mono-cyclometalated compounds apply for the bis-cyclometalated compounds structurally characterized. The metalated rings are planar and retain the sequence of short−long−short C−C bond distances. In all cases, the sulfur atoms in the metalated rings were unambiguously located. Some nonmetalated thienyl rings presented disorder and were refined as previously described for **2A** and **2B**.

As expected, in the bis-cyclometalated compounds the rhodium−rhodium bond distances are longer than for monometalated compounds [**3AA**, 2.5155(5) Å] and increase when replacing acetic acid by pyridine in axial positions in the case of **4AA·py** [2.5413(6) Å] or by one phosphine in **4AA·1** [2.5845(9) Å]. In addition, the head-to-head compound with axial ligands, **4AA·py**, presents distorted metalocycles, with P−Rh−Rh−C torsion angles of 15.2(2)° and 21.4(2)° and O−Rh−Rh−O of 16.2(2) Å. The ORTEP drawing for these bis-cyclometalated compounds are included in the Supporting Information (Figures S9−S11).

**Table 1. $^{31}P\{^1H\}$ NMR Data for the Mono- and Bis-cyclometalated Dirhodium(II) Compounds**

| compound | $\delta P_1(^1J_{Rh1-P1};\ ^2J_{Rh2-P1})^b$ | $\delta P_2(^1J_{Rh2-P2};\ ^2J_{Rh1-P2};\ ^3J_{P1-P2})^b$ | $\delta P_3(^1J_{Rh2-P2};\ ^2J_{Rh1-P2};\ ^3J_{P1-P3})^c$ |
|---|---|---|---|
| **2A** | 0.6 (158.0; 6.0) | | |
| **2B** | −3.0 (154.0; 3.1) | | |
| **3AA**[a] | 4.4 (177.0; −7.0) | | |
| **3AB** | 1.1 (171.5; 7.2) | −2.3 (171.6; 6.7; −) | |
| **3BB**[a] | −0.5 (165.5; −9.5) | | |
| **4AA** | 2.4 (158.0; 7.5) | | |
| **4AB** | 4.4 (158.7; 7.6) | −2.3 (156.4; 6.9; 44.7) | |
| **4BB** | −1.0 (156.0; 7.0) | | |
| **4AA·1** | 4.9 (160.5; 2.0) | | −15.3 (138.0; 32.0; 8.9) |
| **4AB·1** | 5.1 (161.0; 3.0) | 2.0 (158.0; 2.5; 43.3) | −25.5 (114.0;36.8;10.0) |
| **4BB·1** | 2.3 (159.0; 2.5) | | −25.6 (124.0; 37.2; 9.1) |

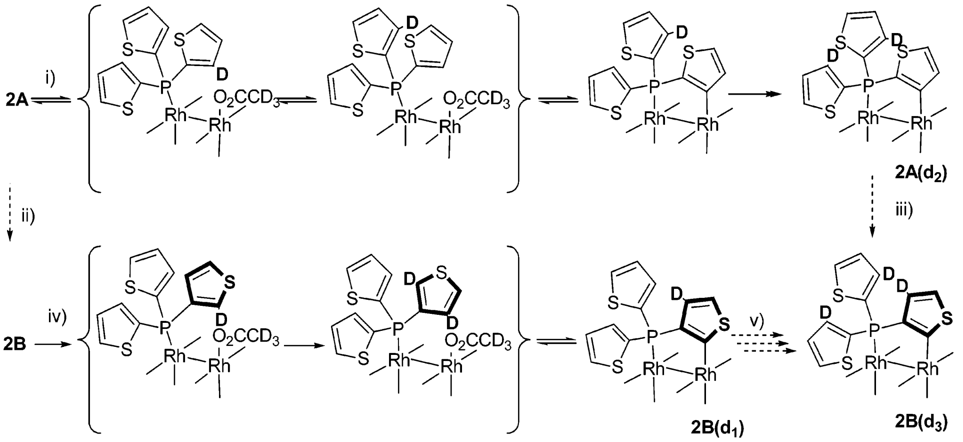
[a] Coupling constants *J* were obtained by spectra simulation using gNMR software (for $^3J_{P1-P2}$ and $^1J_{Rh1-Rh2}$ values see the Experimental Section). [b] Signals due to the metalated phosphines. [c] Signals due to the axial phosphine.

Compound **4BB** had been previously characterized.[12] All the efforts to obtain single crystals from **4BB·1** failed. Surprisingly, crystals from a solution that contained a mixture of **4AB·1** and **4BB·1** were obtained by serendipity. To confirm the ability of the X-ray methods to detect disorder in the positions of sulfur atoms, we measured and solved the crystal structure of one of those crystals (Figure S12 in SI). One of the metalated rings refined well, assuming only a structure of type **B**, but some disorder in the metalated ring was clearly detected in the second phosphine. The best refinement was obtained assuming structure of type **B** in one of the rings, while the second ring refined better for 53% occupancy as structure of type **A** and 47% as structure of type **B**. That product distribution was roughly confirmed by a $^{31}P$ NMR spectrum collected on the measured single crystal.

**NMR Studies.** All the isolated compounds were studied by multinuclear $^1H$, $^{31}P$, and $^{13}C$ NMR spectroscopy. The data allowed us to establish the stoichiometry of each compound as mono- or bis-cyclometalated. Compounds with phosphines in a head-to-tail configuration (**3AA** or **3BB**) show a second-order AA′XX′ spectrum in the $^{31}P$ NMR spectrum, while those with head-to-head structure (like **4AA** or **4BB**) have a simpler $A_2$-XX′ pattern of signals. As expected, nonsymmetrical compounds with two different phosphines (**3AB** or **4AB**) exhibit two set of signals in their $^{31}P$ NMR spectrum (Table 1). All these compounds exhibit chemical shift values in a narrow range, the signal due to phosphines in structure type **B** shielded by ca. 3−5 ppm compared with those signals in structure type **A**.

The spectroscopic location of the sulfur atoms within the thienyl rings is not straightforward. In the following, we will describe the case of the simple mono-cyclometalated compounds **2A** and **2B**. They have five different protons in the aromatic region, and COSY experiments allowed an unambiguous assignment of them. The structural identification of the compounds, as having structure **A** or **B**, has been done on the basis that in the metalated rings compounds with structure **B** have a proton at three bonds from phosphorus, while in compounds with structure **A** the minimum separation is four bonds. However, the nonmetalated rings always have protons at three bonds from phosphorus in both situations. Therefore, structural

**Scheme 3. H/D Exchange by Thermal Treatment of 2A or 2B in Deuterated Acetic Acid**



i) 70° C, $CD_3CO_2\mathbf{D}$, 2.5 h, ii) Refluxing $CH_3CO_2H$, 20 h; iii) 70° C, $CD_3CO_2\mathbf{D}$, 32.5 h; iv) 70° C, $CD_3CO_2\mathbf{D}$, 2 h; v) 70° C, $CD_3CO_2\mathbf{D}$, 50 h

differentiation was successfully performed by a combination of COSY experiments (to assign the signals due to the protons in the metalated and nonmetalated rings) and HMBC $^1H-^{31}P$ spectra. By this procedure, we have been able to structurally identify those compounds that did not allow X-ray crystal structure determination. The method was successfully tested with compounds **2A**/**2B** and **4AA**/**4BB**, whose structure were determined by X-ray analysis. The results for the bis-cyclometalated compounds support the structural assignment made for these compounds (see Figures S3 and S4 in SI).

**Thermal Treatment with $CD_3CO_2D$. Compound 2A.** Aiming to have more information about this particular ring rearrangement process, the transformation from **2A** to **2B** was monitored by $^1H$ NMR spectroscopy, using $CD_3CO_2D$ as solvent (Scheme 3). We first observed a rapid exchange of $CH_3CO_2$ by $CD_3CO_2$ groups that was complete in 15 min at 70 °C. Such particular exchange has been previously reported for an analogous dirhodium(II) compound with metalated triphenylphosphine, $Rh_2(O_2CCH_3)_3[(C_6H_4)PPh_2](CH_3CO_2H)_2$.[15]

After 2.5 h under the above-described conditions, compound **2A** experienced selective and complete H/D exchange at the carbon atom C-3 in the two nonmetalated rings of the phosphine, yielding species **2A(d$_2$)** (Scheme 3). This exchange, already observed for other cyclometalated rhodium(II) compounds,[15] was explained by electrophilic cleavage of the Rh−C bond of the metalated phosphine followed by carbon−hydrogen bond activation. Rapid rotation around the Rh−P bond in the demetalated species would allow deuteration of all the thienyl rings at the C-3 position.

We confirmed that for compound **2A** H/D exchange and ring rearrangement occurred with very different rates, the later being considerably slower. Thus, while the H/D exchange was complete in **2A** after 2.5 h to give **2A(d$_2$)**, the complete rearrangement of **2A** to **2B** required more than 35 h of reaction at the same temperature (70 °C). The resulting species was **2B-(d**$_3$) (Scheme 3), which incorporated one additional deuterium atom at the metalated ring.

The incorporation of the deuterium into the metalated ring is not associated with the rearrangement process itself, but it occurs on the rearranged product. Thus, after heating a solution of **2B** in $CD_3CO_2D$ at 70 °C for 2 h, selective H/D exchange was observed by $^1H$ NMR spectroscopy, yielding compound **2B-(d$_1$)** as the only species in solution.

This particular H/D exchange in the metalated ring of **2B** can be explained by electrophilic cleavage of the Rh−C bond, followed by cyclometalation reaction. The 3-thienyl ring has two carbon atoms that can experience cyclometalation, and consequently, compounds with structure type **B** or **C** (Scheme 1) can be generated. The last type of metalocycle, not detected in solution, must be responsible for the H/D exchange observed in **2B**. The fact that only **2B(d$_1$)** was observed in solution is in agreement with the lower energy (−24 kJ/mol) calculated for this compound compared to the isomer with structure type **C**, not detected in these conditions. The incorporation of deuterium in all the thienyl rings, from **2B(d$_1$)** to **2B(d$_3$)**, was also possible, but required more than 50 h of thermal treatment.

It is remarkable that H/D exchange at the nonmetalated thienyl rings is considerably slower in **2B** than in **2A**. Although there is not a simple explanation for that, the higher facility to experience C−H activation in 3-thienyl rings, compared to 2-thienyl rings, could be invoked to explain this observation.

**Compounds 3AA and 4AA.** We also studied the chemical evolution of compound **3AA** in $CD_3CO_2D$. In addition to rapid exchange of $CH_3CO_2$ by $CD_3CO_2$ groups, selective H/D exchange was observed, which takes place at a much slower rate than for **2A**. Signals assignable to **3AB** and **3BB** were also observed in the spectrum before a significant H/D was detected. Under the same conditions, compound **4AA** led to the evolution of **4BB**, with the intermediate **4AB** also being detected. That process is faster than for **3AA**. However, the spectra at the intermediate states were too complicated, and because of that, the H/D exchange could not be monitored.

From these experiments we can establish that in **3AA** the rearrangement is considerably slower than in the two other compounds. We can also conclude that, at least in **2A** and **3AA**, the rearrangement and the Rh−C bond cleavage follow different rates, suggesting that the rearrangement does not involve cleavage of the Rh−C bond at the rate-determining step.

We should finally mention that the uncoordinated ligand **1** does not experience any rearrangement under the same conditions in which the metalated compounds do.

## Computational Results

Density functional theoretical (DFT) calculations were performed to determine the relative energies for the above-described thienyl compounds. The energy values calculated for the optimized structures of key compounds are shown in Table 2.

---

[15] Lahuerta, P.; Peris, E. *Inorg. Chem.* **1992**, *31*, 4547.

**Table 2. Calculated Relative Energies for Selected Dirhodium(II) Complexes**[a]

| compound | Δ*E* (kJ/mol) |
|---|---|
| Mono-cyclometalated | |
| **2A** | 0 |
| **2B** | −15.8 |
| Bis-cyclometalated | |
| **3AA** | −24.9 |
| **3AB** | −41.8 |
| **3BB** | −57.5 |
| **4AA** | 0 |
| **4AB** | −15.9 |
| **4BB** | −33.6 |

[a] The energies (kJ/mol) are referenced to the underlined compound in each series.

Bis-cyclometalated compounds with phosphines in a head-to-tail arrangement are about 25 kJ/mol more stable than the corresponding head-to-head compounds. These results are in agreement with the observed thermal evolution from the head-to-head to the head-to-tail isomers.

Data in Table 2 also indicate that the first change in the metalated thienyl ring, from structure **A** to **B**, represents a stabilization of ca. 16 kJ/mol per ring for the mono-cyclometalated or bis-cyclometalated pairs (**2A**/**2B**, **3AA**/**3AB**, **4AA**/**4AB**). The rearrangement of the second metalated ring in the bis-cyclometalated compounds produced similar stabilization (compare energies in **3AB**/**3BB**, **4AB**/**4BB** pairs). These calculations confirmed that the thermal evolution observed for some of these compounds in strong acid medium is driven by thermodynamic factors, meanwhile kinetic factors make these processes take place with quite different rates.

Also, the calculated interatomic distances in compounds **2A** and **2B** were in good agreement with those obtained by X-ray analysis. Only the calculated Rh−P bond distances were longer (1.6 to 1.8%) than those determined by X-ray analysis (see Table S4 in SI).

The energy differences are rather small, as they often are when considering isomerization reactions. However, the trends they present are consistent with the experiments. Although the reported energies have been calculated without any temperature corrections, we have performed free energy calculations on the key steps of the mechanism (323 K). The results do not show any change in the obtained trend; the free energy differences are a few kJ/mol larger than the total energy differences, which only makes the conclusions more clear. Therefore, thermodynamic calculations at elevated temperature were not repeated for all the compounds.

## Conclusions

We have studied the reactivity of dirhodium(II) tetraacetate with tris(2-thienyl)phosphine.[16−22] We have characterized several species with the phosphine acting as a cyclometalated bridging ligand. No species with the phosphine acting as a P,S donor ligand have been observed, although in some cases this particular coordination has been found.[20]

On the other hand, when coordinated to a metal, the 2-thienyl group is considered to be more electron-donating toward P than the phenyl group.[16] All the results confirm that **1**, in the presence of dirhodium(II) tetraacetate, experiences metalation reaction more readily than triaryl phosphines. This is in good agreement with the electron-rich character of the thienyl compared to phenyl groups. Moreover, the ability to undergo such reactions under photochemical conditions is also remarkable.

For all the isolated compounds, a selective ring rearrangement was observed from cyclometalated structure **A** to **B**. This process, which requires the presence of concentrated acetic acid, is favored in the order **3AA** ≪ **4AA** ∼ **2A**. DFT calculations support that the rearrangement is enthalpy controlled. The role of the metal is apparently important, as no evidence of this process was observed in the free ligand under the same conditions.

In addition, experiments with deuterated acetic acid evidenced that rearrangement does not require a previous Rh−C bond cleavage.

The available data do not allow to make a detailed mechanistic proposal for this isomerization. However, according to natural population analysis (NPA), the highest electron density is located at the carbon atom bonded to phosphorus in the metalocycle. These data suggest protonation of this particular carbon atom as the promoting step of the process yielding structure **I** in Scheme 4. The fact that the negative charge value in this particular carbon atom increases in the order **3AA** ≪ **4AA** ∼ **2A**, as the reactivity order, supports this preliminary assumption. Later on, 1,2-P migration concerted with ring aromatization would lead to structure **III**, able to give rise to structure type **B** after metalation.

## Experimental Section

Commercially available $Rh_2(O_2CCH_3)_4(CH_3OH)_2$ was purchased from Pressure Chemical Co. $P(2\text{-}SC_4H_3)_3$ was prepared by nucleophilic displacement on phosphorus trichloride by the organolithium reagent.[23]

All solvents were of analytical grade. All the irradiations were made with a 125 W mercury lamp with Pyrex filter. $^1H$, $^{13}C$, and $^{31}P$ NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer as solutions in $CDCl_3$ at 25 °C. $^1H$ and $^{13}C$ NMR spectra were referenced to residual solvent peaks. $^{31}P$ were referenced with an external $H_3PO_4$ sample. Chemical shifts are reported in ppm. The coupling constants (*J*) are in hertz (Hz). Coupling constant values for AA′XX′ systems were obtained from simulated spectra. Analyses were provided by Centro de Microanálisis Elemental, Universidad Complutense de Madrid. Column chromatography was performed on silica gel (35−70 mesh). Solvent mixtures are volume/volume mixtures, unless specified otherwise. All reactions were carried out in oven-dried glassware under argon atmosphere, although the isolated solids are air-stable.

**Synthesis of $Rh_2(O_2CCH_3)_3[(2\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2](CH_3CO_2H)_2$ (2A).** A solution of $Rh_2(O_2CCH_3)_4(MeOH)_2$ (251 mg, 0.5 mmol) and **1** (112 mg, 0.4 mmol) in a mixture of toluene/acetic acid (48 mL, 9:1) was refluxed for 2 h. After cooling, the solvent was evaporated under reduced pressure and the resulting purple solid was dissolved in $CH_2Cl_2$/AcOEt (2 mL; 1:1). The product was transferred to a chromatography column packed with silica gel on hexanes. Elution with $CH_2Cl_2$/hexanes/AcOEt (1:2:2) afforded a green band of dirhodium(II) tetraacetate followed by a gray band, which was collected. Crystallization from $CH_2Cl_2$/hexanes and few

---

(16) Allen, D. W.; Ashford, D. F. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1953.

(17) Allen, D. W.; Bell, N. A.; Fong, S. T.; March, L. A.; Nowell, I. W. *Inorg. Chim. Acta* **1985**, *99*, 157.

(18) Barral, M. C.; Jimenezaparicio, R.; Kramolowsky, R.; Wagner, I. *Polyhedron* **1993**, *12*, 903.

(19) Bodensieck, U.; Vahrenkamp, H.; Rheinwald, G.; Stoecklievans, H. *J. Organomet. Chem.* **1995**, *488*, 85.

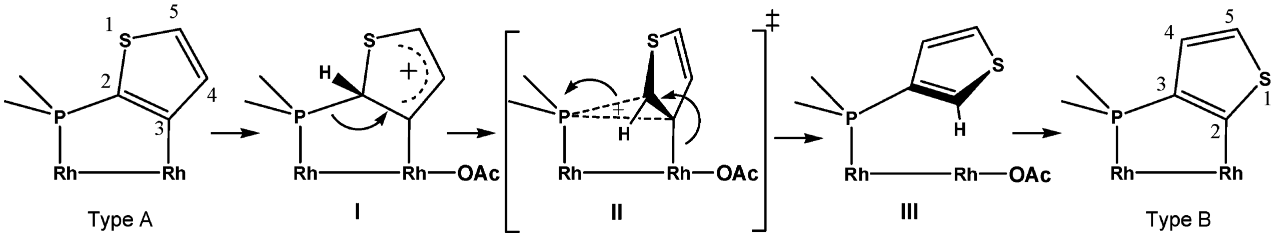
(20) Deeming, A. J.; Jayasuriya, S. N.; Arce, A. J.; DeSanctis, Y. *Organometallics* **1996**, *15*, 786.

(21) Monkowius, U.; Nogai, S.; Schmidbaur, H. *Z. Naturforsch. B* **2003**, *58*, 751.

(22) Rasanen, T. M.; Jaaskelainen, S.; Pakkanen, T. A. *J. Org. Chem.* **1998**, *553*, 453.

(23) Isslieb, K. B., A. *Z. Anorg. Allg. Chem.* **1957**, *292*, 245.

**Scheme 4. Possible Mechanistic Explanation for the Rearrangement from Structures Type A to Type B in Acetic Acid**



drops of acetic acid gave **2**: yield 188 mg (60%) as a gray crystalline product. $^1$H NMR: $\delta$ 1.49 (s, 6H; $CH_3$ *cis*), 2.34 (s, 6H; $CH_3$ *axial*), 2.41 (s, 3H; $CH_3$ *trans*), 7.07 (ddd, $J = 1$ Hz, $J = 3.5$ Hz, $J = 5.0$ Hz, 2H; $C_4H_3S$), 7.46 (ddd, $J = 1$ Hz, $J = 3.5$ Hz, $J = 7.8$ Hz, 2H; $C_4H_3S$), 7.62 (ddd, $J = 1$ Hz, $J = 3.5$ Hz, $J = 4.1$ Hz, 2H; $C_4H_3S$), 7.82 (dd, $J = 2.0$ Hz, $J = 5.0$ Hz, 1H; $C_4H_2S$), 8.08 ppm (dd, $J = 3.0$ Hz, $J = 5.0$ Hz, 1H; $C_4H_2S$). $^{13}C\{^1H\}$ NMR: $\delta$ 21.69 (s), 23.73 (s), 23.85 (d, $J = 3$ Hz), 127.71 (d, $J = 13$ Hz), 130.47 (s), 132.75 (d, $J = 3$ Hz), 133.68 (d, $J = 59$ Hz), 134.38 (d, $J = 29$ Hz), 136.05 (d, $J = 5$ Hz), 165.58 (m, metalated), 179.62 (s), 182.86 (s), 190.101 ppm (s). $^{31}P\{^1H\}$ NMR: $\delta$ 0.6 ppm (dd, $^1J(P-Rh) = 158.0$ Hz, $^2J(P-Rh) = 6.0$ Hz). Anal. Calcd (%) for $C_{22}H_{25}O_{10}PRh_2S_3$ (782.4): C 33.76, H 3.20. Found: C 33.90, H 3.35.

Single crystals of **2A** suitable for X-ray diffraction were obtained by slow evaporation of a solution of the compound in $CH_2Cl_2$/hexane containing two drops of acetic acid.

**X-ray Crystal Structure Data for $Rh_2(O_2CCH_3)_3[(2\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2](CH_3CO_2H)_2$ (2A).** $C_{44}H_{50}O_{20}P_2Rh_4S_6$: monoclinic, space group *P*2(1)/*n*, $a = 16.692(3)$ Å, $b = 10.384(2)$ Å, $c = 33.224(7)$ Å, $\beta = 97.73(3)°$, $V = 5706(2)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.821$ g cm$^{-3}$, crystal dimensions $0.28 \times 0.25 \times 0.25$ mm$^3$; Kappa CCD diffractometer; Mo K$\alpha$ radiation, 293(2) K; 20 296 reflections, 12 319 independent ($\mu = 1.483$ mm$^{-1}$); refinement (on $F^2$) with SHELXTL (version 6.1), 699 parameters, 0 restraints, $R_1 = 0.0593$ ($I > 2\sigma$) and $wR_2$ (all data) = 0.1917, GOF = 0.950, max./min. residual electron density 1.547/$-$1.482 e Å$^{-3}$. There are two independent molecules per asymmetric unit. CCDC-290536 contains the supplementary crystallographic data.

**Synthesis of $Rh_2(O_2CCH_3)_2[(2\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2]_2(CH_3CO_2H)_2$ (3AA). Method A.** A solution of $Rh_2(O_2CCH_3)_4\cdot 2MeOH$ (101 mg, 0.2 mmol) and **1** (120 mg, 0.43 mmol) in $CH_2Cl_2$/acetic acid (100 mL, 9:1) was irradiated for 2.5 h. The solvent was evaporated under reduced pressure, and the resulting purple solid was washed with $Et_2O$ ($3 \times 2$ mL). The remaining solid was crystallized by dissolving in the minimum amount of $CH_2Cl_2$ and layering with a mixture of $Et_2O$/hexanes. A red microcrystalline red solid was separated. Yield: 183 mg (90%).

**Method B.** A solution of $Rh_2(O_2CCH_3)_4(MeOH)_2$ (100 mg, 0.2 mmol) and **1** (120 mg, 0.43 mmol) in a mixture of toluene/acetic acid (40 mL, 9:1) was refluxed for 20 h. After cooling, the solvent was evaporated under reduced pressure and the resulting red solid was dissolved in $CH_2Cl_2/Et_2O$ (1 mL, 9:1). The solution was transferred to a chromatography column packed with silica gel on hexanes. After very slow elution with $CH_2Cl_2/Et_2O$/AcOH (90:10:0.5) a minor red band was discarded followed by a larger red band, which was collected. After evaporation of the solvent the residue was crystallized from $Et_2O$/hexanes to give a crystalline red solid. Yield: 140 mg (68%). $^1$H NMR: $\delta$ 1.63 (s, 6H; $CH_3$ *equatorial*), 2.38 (s, 6H; $CH_3$ *axial*), 6.65 (dd, $J = 2.8$ Hz, $J = 4.9$ Hz, 2H; $C_4H_2S$), 6.95 (m, 2H; $C_4H_3S$), 7.05 (m, 4H; $C_4H_3S$), 7.30 (m, 2H; $C_4H_2S$), 7.41 (dd, $J = 3.3$ Hz, $J = 7.0$ Hz, 2H; $C_4H_3S$), 7.47 ppm (m, 2H; $C_4H_3S$), 7.60 (m, 2H; $C_4H_3S$). $^{13}C\{^1H\}$ NMR: $\delta$ 22.3 (s), 23.3 (d, $J = 3$ Hz), 125.7 (d, $J = 81$ Hz), 126.1 (m), 127.2 (d, $J = 11.3$ Hz), 127.4 (d, $J = 12.0$ Hz), 131.4 (dd, $J = 2.4$ Hz, $J = 34.5$ Hz), 133.8 (d, $J = 18.8$ Hz), 134.2 (d, $J = 9.2$ Hz), 134.9 (d, $J = 9.9$ Hz), 135.8 (d, $J = 55$ Hz); 136.3 (d, $J = 40.7$ Hz), 166.2 (m), 181.0 (s), 181.9 ppm (d, $J = 2.7$ Hz).$^{31}P\{^1H\}$ NMR: $\delta$ 4.4 ppm ($^1J(P-Rh) = 177.0$ Hz, $^1J(Rh-Rh') = 1.5$ Hz, $^2J(P-Rh) = -7.0$ Hz, $^3J(P-P') = 1.5$ Hz; AA′XX′ system). Anal. Calcd (%) for $C_{32}H_{30}O_8P_2Rh_2S_6$ (1014.7): C 38.33, H 3.02. Found: C 38.28, H 3.16.

Single crystals suitable for X-ray diffraction were collected by layering a concentrated solution of **3A** in $CH_2Cl_2$, containing one drop of acetic acid, with a mixture of $Et_2O$/hexanes (10 mL, 4:1).

**X-ray Crystal Structure Data for $Rh_2(O_2CCH_3)_2[(2\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2](CH_3CO_2H)_2$ (3AA).** $C_{32}H_{29}O_8P_2Rh_2S_6$: monoclinic, space group *P*2(1)/*n*, $a = 10.18100(10)$ Å, $b = 35.7520(4)$ Å, $c = 12.84600(10)$ Å, $\beta = 124.2391(6)°$, $V = 3865.49(6)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.721$ g·cm$^{-3}$, crystal dimensions $0.32 \times 0.30 \times 0.30$ mm$^3$; Kappa CCD diffractometer; Mo K$\alpha$ radiation, 293(2) K; 15 192 reflections, 9868 independent; ($\mu = 1.308$ mm$^{-1}$); refinement (on $F^2$) with SHELXTL (version 6.1), 494 parameters, 375 restraints, $R_1 = 0.0543$ ($I > 2\sigma$) and $wR_2$ (all data) = 0.1715, GOF = 1.043, max./min. residual electron density 1.711/$-$1.614 e Å$^{-3}$. One of the thienyl rings is disordered over two sites, which were refined with a common C position. CCDC-290538 contains the supplementary crystallographic data.

**Synthesis of $Rh_2(O_2CCH_3)_2[(2\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2]_2(CH_3CO_2H)_2$ (4AA).** A solution of $Rh_2(O_2CCH_3)_4\cdot 2MeOH$ (100 mg, 0.2 mmol) and **1** (120 mg, 0.43 mmol) in a mixture of toluene/acetic acid (50 mL, 2:1) was heated under reflux for 2.5 h. After cooling, the solvent was evaporated under reduced pressure and the resulting red solid was dissolved in $CH_2Cl_2/Et_2O$ (1 mL, 9:1). The solution was transferred to a chromatography column packed with silica gel on hexanes. After very slow elution with $CH_2Cl_2/Et_2O$/AcOH (90:10:0.5) a red band was collected. Evaporation of the solvent and crystallization from $Et_2O$/hexanes gave a red solid. Yield: 136 mg (67%). $^1$H NMR: $\delta$ 1.60 (s, 6H; $CH_3$ *equatorial*), 2.31 (s, 6H; $CH_3$ *axial*), 6.61 (t, $J = 4.2$ Hz, 2H; $C_4H_3S$), 6.82 (d, $J = 3.3$ Hz, 2H; $C_4H_3S$), 7.05 (t, $J = 4.1$ Hz, 2H; $C_4H_3S$), 7.22 (d, $J = 4.0$ Hz, 2H; $C_4H_3S$), 7.44 (m, 4H; $C_4H_2S$ and $C_4H_3S$), 7.56 ppm (d, $J = 5.1$ Hz, 2H; $C_4H_2S$), 7.62 (d, $J = 5.0$ Hz, 2H; $C_4H_3S$). $^{13}C\{^1H\}$ NMR: $\delta$ 22.61 (s), 23.39 (s), 124.39$-$124.35 (m), 127.26$-$127.41 (m), 128.87 (s), 129.64 (s), 131.72$-$131.78 (d, $J = 2$ Hz), 133.72 (t, $J = 8$ Hz), 135.28 (t, $J = 8$ Hz), 135.52 (t, $J = 5$ Hz), 135.16$-$137.04 (m), 165.65 (m, metalated), 181.79 ppm (s). $^{31}P\{^1H\}$ NMR: $\delta$ 2.4 ppm (dd, $^1J(P-Rh) = 158.0$ Hz, $^2J(P-Rh) = 7.5$ Hz). Anal. Calcd (%) for $C_{32}H_{30}O_8P_2Rh_2S_6$ (1002.7): C 38.33, H 3.02. Found: C 38.41, H 3.12.

**$Rh_2(O_2CCH_3)_2[(2\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2]_2(C_5H_5N)$ (4AA·py).** This adduct was formed in high yield by adding two drops of pyridine to a solution of **4AA** in dichloromethane. After stirring for 10 minutes, the solution was layered with a mixture of hexanes and was allowed to diffuse. Pale red crystals were separated in a quantitative amount and were dried under vacuum.

Single crystals of **4AA·py** suitable for X-ray diffraction methods were obtained by diffusing hexanes into a dichloromethane solution of the product.

**X-ray Crystal Structure Data for $Rh_2(O_2CCH_3)_2[(2\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2]_2(C_5H_5N)$ (4AA·py).** $C_{33}H_{27}NO_4P_2Rh_2S_6$: monoclinic, space group *P*2(1), $a = 10.4500(2)$ Å, $b = 17.7820(4)$ Å, $c = 10.7120(2)$ Å, $\beta = 117.1070(7)°$, $V = 1771.88(6)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 1.802$ g cm$^{-3}$, crystal dimensions $0.28 \times 0.25 \times 0.23$ mm$^3$;

Kappa CCD diffractometer; Mo Kα radiation, 293(2) K; 7348 reflections, 6611 independent; ($\mu = 1.415$ mm$^{-1}$); refinement (on $F^2$) with SHELXTL-NT (version 6.1), 435 parameters, 1 restraint, $R_1 = 0.0417$ ($I > 2\sigma$) and $wR_2$ (all data) $= 0.1240$, GOF $= 1.171$, max./min. residual electron density 0.648/$-$1.002 e Å$^{-3}$. The absolute configuration was established by anomalous dispersion effects in diffraction measurements on the crystal, Flack parameter $-$0.05(4). CCDC-290539 contains the supplementary crystallographic data.

**$Rh_2(O_2CCH_3)_2[(2\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2]_2(P(2\text{-}C_4H_3S)_3)$ (4AA·1).** This adduct was formed in high yield by adding 2 equiv of **1** to a solution of **4AA** in dichloromethane. After stirring for 10 minutes, the solution was layered with a mixture of hexanes and was allowed to diffuse. Orange crystals were separated and were dried under vacuum. $^1H$ NMR: $\delta$ 1.42 (s, 6H; $CH_3$ *equatorial*), 6.58 (m, 2H; $C_4H_2S$), 6.62 (m, 2H; $C_4H_2S$), 6.66 (m, 2H; $C_4H_3S$), 7.06 (m, 2H; $C_4H_3S$), 7.14 (m, 3H; $C_4H_3S$), 7.22 (m, 4H; $C_4H_3S$), 7.55 (d, $J =$ 6 Hz, 2H; $C_4H_3S$), 7.62 (m, 3H; $C_4H_3S$), 7.66 (m, 2H; $C_4H_3S$), 7.87 ppm (m, 3H; $C_4H_3S$). $^{31}P\{^1H\}$ NMR: $\delta$ 4.9 (ddd, $^1J(P_{met}-Rh) = 160.5$ Hz, $^2J(P_{met}-Rh) = 2.0$ Hz, $^3J(P_{met}-P_{ax}) = 8.9$ Hz; $P_{met}$), $-15.3$ ppm (ddt, $^1J(P_{ax}-Rh) = 138$ Hz, $^2J(P_{ax}-Rh) = 32$ Hz, $^3J(P_{ax}-P_{met}) = 8.9$ Hz; $P_{ax}$).

Single crystals of **4AA·1** suitable for X-ray diffraction methods were obtained by diffusing hexanes into a dichloromethane solution of the product.

**X-ray Crystal Structure Data for $Rh_2(O_2CCH_3)_2[(2\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2]_2(P(2\text{-}C_4H_3S)_3)$ (4AA·1).** $C_{40}H_{31}O_4P_3Rh_2S_9$: triclinic, space group $P\bar{1}$, $a = 10.0120(2)$ Å, $b = 13.6760(2)$ Å, $c = 18.4170(3)$ Å, $\alpha = 94.5960(9)°$, $\beta = 96.8350(11)°$, $\gamma = 101.3200(9)°$, $V = 2441.19(7)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 1.669$ g cm$^{-3}$, crystal dimensions $0.35 \times 0.32 \times 0.25$ mm$^3$; Kappa 2000 diffractometer; Cu Kα radiation, 293(2) K; 7733 reflections, 5475 independent ($\mu = 10.389$ mm$^{-1}$); refinement (on $F^2$) with SHELXTL (version 6.1), 571 parameters, 12 restraints, $R_1 = 0.0829$ ($I > 2\sigma$) and $wR_2$ (all data) $= 0.2295$, GOF $= 1.024$, max./min. residual electron density 1.484/$-$1.230 e Å$^{-3}$. Hydrogen atoms of water molecules were not found. One of the thienyl rings is disordered over two sites, which were refined with a common C position. All C atoms belonging to both disorder components were refined isotropically. CCDC-290540 contains the supplementary crystallographic data.

**Synthesis of $Rh_2(O_2CCH_3)_3[(3\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2](CH_3CO_2H)_2$ (2B).** A solution of **2A** (100 mg, 0.13 mmol) in acetic acid (10 mL) was refluxed for 20 h. After cooling, the solution was concentrated under reduced pressure and the concentrated solution was layered with 5 mL of $Et_2O$. A green microcrystalline solid was separated: Yield: 85 mg (85%). $^1H$ NMR: $\delta$ 1.59 (s, 6H; $CH_3$ *equatorial-cis*), 2.15 (s, 3H; $CH_3$ *equatorial-trans*), 2.20 (s, 6H; $CH_3$ *axial*), 7.07 (m, 2H; $C_4H_3S$), 7.34 (m, 1H; $C_4H_2S$), 7.45 (m, 1H; $C_4H_2S$), 7.48 (m, 2H; $C_4H_3S$), 7.61 ppm (m, 2H; $C_4H_3S$). $^{13}C\{^1H\}$ NMR: $\delta$ 20.76 (s), 23.64 (s), 23.74 (m), 126.31 (d, $J =$ 13 Hz), 127.72 (d, $J = 13$ Hz), 127.80 (d, $J = 12$ Hz), 128.37 (d, $J = 11$ Hz), 132.42 (d, $J = 3$ Hz), 133.37 (d, $J = 56$ Hz), 135.73 (d, $J = 10$ Hz), 136.52 (s), 168.57 (m, metalated), 177.78 (s), 183.43 (s), 190.32 ppm (s). $^{31}P\{^1H\}$ NMR: $\delta$ $-3.0$ (dd, $^1J(P-Rh) = 154.0$ Hz, $^2J(P-Rh) = 3.1$ Hz). Anal. Calcd (%) for $C_{22}H_{25}O_{10}PRh_2S_3$ (782.4): C 33.76, H 3.20. Found: C 33.83, H, 3.28.

Single crystals of **2B** suitable for X-ray diffraction were obtained by slow evaporation of a concentrated solution of the product in acetic acid.

**X-ray Crystal Structure Data for $Rh_2(O_2CCH_3)_3[(2\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2]$ $(CH_3CO_2H)_2$ (2B).** $C_{22}H_{25}O_{10}PRh_2S_3$: monoclinic, space group $P2(1)$, $a = 8.5790(2)$ Å, $b = 18.2770(5)$ Å, $c = 9.3080(3)$ Å, $\beta = 93.8070(11)°$, $V = 1456.26(7)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 1.773$ g cm$^{-3}$, crystal dimensions $0.30 \times 0.27 \times 0.25$ mm$^3$; Kappa CCD diffractometer; Mo Kα radiation, 293(2) K; 5567 reflections, 4832 independent ($\mu = 1.453$ mm$^{-1}$); refinement (on $F^2$) with SHELXTL (version 6.1), 347 parameters, 1 restraint, $R_1 = 0.0434$ ($I > 2\sigma$) and $wR_2$ (all data) $= 0.1059$, GOF $= 1.082$, max./min. residual electron density 0.705/$-$0.884 e Å$^{-3}$. The absolute configuration was established by anomalous dispersion effects in diffraction measurements on the crystal, Flack parameter 0.02(5). CCDC-290537 contains the supplementary crystallographic data.

**Synthesis of $Rh_2(O_2CCH_3)_2[(2\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2][(3\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2]$ $(CH_3CO_2H)_2$ (3AB). Method A.** A solution of $Rh_2(O_2CCH_3)_4{\cdot}2MeOH$ (100 mg, 0.2 mmol) and **1** (120 mg, 0.43 mmol) in acetic acid (50 mL) was refluxed for 20 h. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed the presence in solution of compounds **2B**, **3AA**, **3AB**, **3BB**, and **4BB** with spectroscopic yields of 8, 20, 40, 10, and 12%, respectively, plus 10% of phosphine oxide. After cooling, the solvent was evaporated under reduced pressure and the resulting red solid was dissolved in $CH_2Cl_2/Et_2O$ (1 mL, 9:1). The solution was transferred to a chromatography column packed with silica gel on hexanes. After very slow elution with $CH_2Cl_2/Et_2O/AcOH$ (90:10:0.5) a red band, mainly containing compound **4BB**, was discarded. Subsequently, a red band was collected and the residue after concentration under reduced pressure was transferred to a chromatography column packed with silica gel on hexanes. After very slow elution with $CH_2Cl_2/Et_2O/AcOH$ (90:10:0.5) this sample, mainly containing **3AB**, was purified from a small amount of **3BB**. After evaporation of the solvent the residue was crystallized from diethyl ether/hexanes to give a red crystalline solid. Yield: 60 mg (30%). No other bands were collected from this experiment.

**Method B.** A solution of **3AA** (100 mg, 0.1 mmol) in neat acetic acid (10 mL) was refluxed for 20 h. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed the presence in solution of compounds **3AA**, **3AB**, and **3BB** with spectroscopic yields of 26, 48, and 12%, respectively, plus 9% of compound **2B** and 5% of phosphine oxide. After cooling, the solvent was evaporated under reduced pressure and the resulting red solid was dissolved in $CH_2Cl_2/Et_2O$ (1 mL, 9:1). The solution was transferred to a chromatography column packed with silica gel on hexanes. After very slow elution with $CH_2Cl_2/Et_2O/AcOH$ (90:10:0.5) a main red band was collected containing an impure sample of **3AB**. A complete purification required a second chromatography under the same conditions. After evaporation of the solvent the residue was crystallized from diethyl ether/hexanes to give a red crystalline solid. Yield: 40 mg (40%). No other bands were collected from this experiment.

**Method C.** A solution of **2B** (50 mg, 0.064 mmol) and **1** (18.5 mg, 0.066 mmol) in $CH_2Cl_2$/acetic acid (10 mL, 9:1) was irradiated for 20 min. The solvent was evaporated under reduced pressure, and the resulting purple solid was washed with $Et_2O$ ($3 \times 2$ mL). The remaining solid was crystallized by dissolving in the minimum amount of $CH_2Cl_2$ and layering with a mixture of $Et_2O$/hexanes. A red solid was separated. Yield: 53 mg (80%). $^1H$ NMR: $\delta$ 1.64 (s, 3H, $CH_3$ *equatorial*), 1.68 (s, 3H, $CH_3$ *equatorial*), 2.44 (s, 6H, $CH_3$ *axial*), 6.24 (m, 1H, $C_4H_2S$), 6.34 (d, $J = 2.5$ Hz, 1H, $C_4H_3S$), 6.60 (m, 4H), 6.73 (m, 5H), 6.81 (m, 2H), 7.17 (m, 2H), 7.31 (dd, $J = 7.5$ Hz, $J = 3.5$ Hz, 1H). $^{31}P\{^1H\}$ NMR: $\delta$ 1.1 (dd, $^1J(P_A-Rh) = 171$ Hz, $^2J(P_A-Rh) = 7$ Hz, $P_A$), $-2.3$ (dd, $^1J(P_B-Rh) = 172$ Hz, $^2J(P_B-Rh) = 6.7$ Hz, $P_B$). Anal. Calcd (%) for $C_{32}H_{30}O_8P_2S_6Rh_2$ (1002.7): C 38.33, H 3.02. Found: C 38.23, H 3.22.

All the efforts to obtain single crystals of **3AB** suitable for X-ray diffraction failed.

**Synthesis of $Rh_2(O_2CCH_3)_2[(3\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2]_2(CH_3CO_2H)_2$ (3BB). Method A.** A solution of $Rh_2(O_2CCH_3)_4{\cdot}2MeOH$ (100 mg, 0.2 mmol) and **1** (120 mg, 0.43 mmol) in acetic acid (50 mL) was refluxed for 170 h. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed the presence in solution of compounds **3AB** and **3BB** in a 1:4 ratio. After cooling, the solvent was evaporated under reduced pressure, and the resulting red solid was dissolved in $CH_2Cl_2/Et_2O$ (1 mL, 9:1). The solution was transferred to a column of chromatography packed with silica gel on hexanes. After very slow elution with $CH_2Cl_2/Et_2O/AcOH$ (90:10:0.5) a red band was discarded followed by a red band that was collected. After evaporation of the solvent, the residue was crystallized from diethyl ether/hexanes to give a red crystalline solid. Yield: 40 mg (20%).

**Method B.** A solution of **3AA** (100 mg, 0.1 mmol) in acetic acid (10 mL) was refluxed for 150 h. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed the presence in solution of compounds **3AB** and **3BB** with spectroscopic yields of 15% and 48%, respectively. The presence of other not characterized compounds and phosphine oxide was also detected. After cooling, the solvent was evaporated under reduced pressure and the resulting red solid was dissolved in $CH_2Cl_2/Et_2O$ (1 mL, 9:1). The solution was transferred to a chromatography column packed with silica gel on hexanes. After very slow elution with $CH_2Cl_2/Et_2O/AcOH$ (90:10:0.5), a red band was discarded followed by a second red band that was collected. After evaporation of the solvent the residue was crystallized from diethyl ether/hexanes to give a red crystalline solid. Yield: 30 mg (30%). $^1H$ NMR: $\delta$ 1.22 (s, 6H; $CH_3$ *equatorial*), 2.14 (s, 6H; $CH_3$ *axial*), 6.98 (m, 2H; $C_4H_3S$), 7.00 (d, $J = 5.1$ Hz, 2H; $C_4H_2S$), 7.03 (d, $J = 7.3$ Hz, 2H; $C_4H_3S$), 7.08 (m, 2H; $C_4H_3S$), 7.13 (d, $J = 4.9$ Hz, 2H; $C_4H_2S$), 7.52−7.45 (m, 4H; $C_4H_2S$ and $C_4H_3S$), 7.56 ppm (m, 2H; $C_4H_3S$). $^{13}C\{^1H\}$ NMR: $\delta$ 20.97 (s), 26.92 (s), 127.06 (d, $J = 13$ Hz), 127.48 (m), 128.72 (m), 131.20 (t, $J = 2.5$ Hz), 134.09 (d, $J = 9$ Hz), 135.00 (d, $J = 71$ Hz), 135.02 (d, $J = 10$ Hz), 135.23 (d, $J = 12$ Hz), 135.42 (d, $J = 59$ Hz), 136.40 (d, $J = 79$ Hz), (169.15 (m, metalated), 178.06 (s), 182.35 ppm (s). $^{31}P\{^1H\}$ NMR: $\delta$ −0.5 ppm ($^1J(P-Rh) = 165.5$ Hz, $^1J(Rh-Rh') = 18$ Hz, $^2J(P-Rh) = -9.5$ Hz, $^3J(P-P') = 4.5$ Hz; AA′XX′ system). Anal. Calcd (%) for $C_{32}H_{30}O_8P_2Rh_2S_6$ (1002,7): C 38.33, H 3.02. Found: C 38.15, H, 3.22.

All the efforts to obtain single crystals of **3BB** suitable for X-ray diffraction failed.

**Synthesis of $Rh_2(O_2CCH_3)_2[(2\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2][(3\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2](CH_3CO_2H)_2$ (4AB).** A solution of $Rh_2(O_2CCH_3)_4\cdot 2MeOH$ (300 mg, 0.59 mmol) and **1** (360 mg, 1.27 mmol) in a mixture of toluene/acetic acid (75 mL, 2:1) was heated under reflux for 2.5 h. After cooling, the solvent was evaporated under reduced pressure and the resulting red solid was dissolved in $CH_2Cl_2/Et_2O$ (1 mL, 90:10:0.5). The solution was transferred to a chromatography column packed with silica gel on hexanes. After very fast elution with the same mixture of solvents a red band containing **3AA** and **4AA** was collected (spectroscopic yield 25% and 75%, respectively). The mixture was dissolved in acetic acid (10 mL) and heated to 110 °C for 10 h. After cooling, the solvent was evaporated under reduced pressure and the resulting red solid was dissolved in $CH_2Cl_2/Et_2O$ (1 mL, 9:1). The solution was transferred to a chromatography column packed with silica gel on hexanes. After very slow elution with $CH_2Cl_2/Et_2O/AcOH$ (90:10:0.5) the first red band was collected. After concentration, the residue was transferred again to a column and was eluted with the same solvent mixture. The first eluted band was discarded and the second red band was collected. After evaporation of the solvent, the residue was crystallized from diethyl ether/hexanes to give a red crystalline solid. Yield: 178 mg (30%). $^1H$ NMR: $\delta$ 1.58 (s, 3H; $CH_3$ *equatorial-trans* $P_B$), 1.72 (s, 3H; $CH_3$ *equatorial-trans* $P_A$), 2.2 (s, 6H; $CH_3$ *axial*), 6.52 (m, 1H; ring 1, $P_B$ $C_4H_3S$), 6.61 (m, 1H; ring 1, $P_B$ $C_4H_3S$), 6.69 (m, 1H; ring 2, $P_A$ $C_4H_3S$), 6.92−6.97 (m, 1H+1H; (ring 4, $P_A$ $C_4H_3S$) + (ring 3, $P_B$ $C_4H_2S$)), 7.09 (m, 1H; ring 5, $P_B$ $C_4H_3S$), 7.11−7.15 (m, 1H+1H; (ring 1, $P_B$ $C_4H_3S$) + (ring 4, $P_A$ $C_4H_3S$)), 7.17 (m, 1H; ring 3, $P_B$ $C_4H_2S$), 7.20 (m, 1H, ring 2; $P_A$ $C_4H_3S$), 7.30 (m, 1H; ring 2, $P_A$ $C_4H_3S$), 7.51 (m, 1H; ring 4, $P_A$ $C_4H_3S$), 7.55 (m, 2H; ring 5, $P_B$ $C_4H_3S$), 7.62 ppm (m, 2H; ring 6, $P_A$ $C_4H_2S$). $^{13}C\{^1H\}$ NMR: $\delta$ 20.87 (b), 124.17 (m), 124.71 (d, $J = 13$ Hz), 125.0−125.2 (m), 127.1−127.6 (m), 129.05 (m), 129.25 (m), 129.41 (m), 129.56 (m), 131.18 (d, $J = 2$ Hz), 131.43 (s), 131.60 (s), 131.79−131−90 (m), 134.01 (s), 134.21 (s), 134.54−134.80 (m), 135.19 (d, $J = 10$ Hz), 135.55−136.03 (m), 136.30 (s), 137.11 (s), 137.76 (s), 138.29 (s), 166.50 (m, metalated) 169.95 (m, metalated), 177.86 (s), 181.99 (s), 182.50 ppm (m). $^{31}P\{^1H\}$ NMR: $\delta$ 4.4 (ddd, $^1J(P_A-Rh) = 158.7$ Hz, $^2J(P_A-Rh) = 8$ Hz, $^3J(P_A-P_B) = 45$ Hz; $P_A$), −2.3 ppm (ddd, $^1J(P_B-Rh) = 156$ Hz, $^2J(P_B-Rh) = 7$ Hz, $^3J(P_B-P_A) = 45$ Hz; $P_B$). Anal. Calcd (%) for $C_{32}H_{30}O_8P_2S_6Rh_2$ (1002,7): C 38.33, H 3.02. Found: C 38.28, H 3.16.

All the efforts to obtain single crystals of **4AB** suitable for X-ray diffraction failed. The only single crystals suitable for X-ray diffraction were obtained from a solution containing a mixture of **4AB·**1 and 4BB·1.

**Synthesis of $Rh_2(O_2CCH_3)_2[(3\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2]_2(CH_3CO_2H)_2$ (4BB).** A solution of $Rh_2(O_2CCH_3)_4\cdot 2MeOH$ (100 mg, 0.2 mmol) and **1** (120 mg, 0.43 mmol) in acetic acid (50 mL) was refluxed for 4.5 h. After cooling, the solvent was evaporated under reduced pressure and the resulting red solid was dissolved in $CH_2Cl_2/Et_2O$ (1 mL, 9:1). The solution was transferred to a chromatography column packed with silica gel on hexanes. After very slow elution with $CH_2Cl_2$/ $Et_2O/AcOH$ (90:10:0.5) a red band was collected followed closely by a red band that was discarded. After evaporation of the solvent the residue was crystallized from diethyl ether/hexanes to give a red crystalline solid. Yield: 50 mg (25%). The remaining bands were discarded. $^1H$ NMR: $\delta$ 1.60 (s, 6H; $CH_3$ *equatorial*), 2.10 (s, 6H; $CH_3$ *axial*), 6.58 (t, $J = 4$ Hz 2H), 6.87 (m, 2H), 6.99 (m, 4H), 7.19 (m, 4H), 7.24 (m, 2H), 7.43 ppm (m, 2H). $^{13}C\{^1H\}$ NMR: $\delta$ 14.91 (s), 20.67 (s), 125.1 (m), 127.20−127.45 (m), 128.87−129.00 (m), 131.437 (s), 131.62 (s), 131.51 (d, $J = 18$ Hz), 134.33 (d, $J = 27$ Hz), 134.68 (t, $J = 5$ Hz), 135.10−135.53 (m), 135.86 (t, $J = 6$ Hz), 136.16 (s), 136.57 (s), 136.93 (d, $J = 14$ Hz), 177.66 (s), 182.63 ppm (s). $^{31}P\{^1H\}$ NMR: $\delta$ −1.0 ppm (dd, $^1J(P-Rh) = 156$ Hz, $^2J(P-Rh) = 7$ Hz). Anal. Calcd (%) for $C_{32}H_{30}O_8P_2Rh_2S_6$ (1002.7): C 38.29, H 3.08. Found: C 38.28, H 3.16.

**$Rh_2(O_2CCH_3)_2[(3\text{-}C_4H_2S)P(2\text{-}C_4H_3S)_2]_2(P(2\text{-}C_4H_3S)_3)$ (4BB·1).** This adduct was formed in high yield by adding 2 equiv of **1** to a solution of **4BB** in dichloromethane. After stirring for 10 min, the solution was layered with a mixture of hexanes and allowed to diffuse. Orange crystals were separated and dried in a vacuum. $^1H$ NMR: $\delta$ 1.30 (s, 6H, $CH_3$ *equatorial*), 6.53 (m, 4H), 6.80 (m, 1H), 6.96 (m, 4H), 7.05 (m, 2H), 7.11 (m, 4H), 7.32 (m, 1H), 7.45 (m, 2H), 7.53 (m, 4H), 7.70 (m, 1H) 7.74 (m, 4H). $^{31}P\{^1H\}$ NMR: $\delta$ 2.3 ppm (ddd, $^1J(P_{met}-Rh) = 159$ Hz, $^2J(P_{met}-Rh) = 2$ Hz, $^3J(P_{met}-P_{ax}) = 9$ Hz, $P_{met}$), −25.6 ppm (ddt, $^1J(P_{ax}-Rh) = 124$ Hz, $^2J(P_{ax}-Rh) = 37$ Hz, $^3J(P_{ax}-P_{met}) = 9$ Hz, $P_{ax}$).

Single crystals of **4BB·1** suitable for X-ray diffraction methods were directly obtained by the above-described synthetic method.

**X-ray Crystal Structure Data for 4BB·1.** $C_{43}H_{36}Cl_2O_6P_3Rh_2S_9$: triclinic, space group $P\bar{1}$, $a = 11.4950(2)$ Å, $b = 13.4730(3)$ Å, $c = 18.2790(4)$ Å, $\alpha = 86.7570(12)°$, $\beta = 78.4940(11)°$, $\gamma = 67.1740(11)°$, $V = 2556.10(9)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 1.698$ g cm$^{-3}$, crystal dimensions 0.27 × 0.25 × 0.24 mm$^3$; Kappa CCD diffractometer; Mo K$\alpha$ radiation, 293(2) K; 14 914 reflections, 8096 independent ($\mu = 1.257$ mm$^{-1}$); refinement (on $F^2$) with SHELXTL (version 6.1), 692 parameters, 618 restraints, $R_1 = 0.0754$ ($I > 2\sigma$) and $wR_2$ (all data) = 0.1984, GOF = 1.036, max./min. residual electron density 1.148/−1.152 e Å$^{-3}$. Three of the thienyl rings are disordered over two sites, which were refined with a common C position, in the case of free rings and two C positions in the metalated ring. All the atoms belonging to the disorder components were also refined anisotropically. CCDC-290541 contains the supplementary crystallographic data.

**Computational Details.** All calculations were carried out with the Gaussian98 program package.[24] The DFT level of theory with the nonlocal density functional B3PW91[25,26] was selected for the quantum chemical studies. The basis set was comprised of the Stuttgart-Dresden effective small core potential[27] augmented with an extra p-polarization function for rhodium (SDD(p)), and a standard all-electron basis set 6-31G* for other atoms. Frequency analysis with no scaling was performed to ensure ground-state optimization. The structures were calculated as adducts with two molecules of water in axial positions. For compound **2**, no important energy differences were found when using either acetic acid or water as axial ligands.

Crystal structure data for **2A**, **2B**, **3AA**, **4AA·1**, **4AA·py**, **4BB·1**, and **4AB·1**/**4BB·1** can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif.

**Acknowledgment.** Financial support from Spanish Government (Project MAT2002-0442-1-C02-02 and J. Lloret Fellowship) is gratefully acknowledged. M.S. thanks Dr. M. C. Ramírez de Arellano for very helpful discussions.

**Supporting Information Available:** COSY and HMBC $^{1}H-^{31}P$ spectra for compound **2A**, **2B**, **3AA**, **4AA**, and **4BB** together with additional data on product distribution upon thermal treatment of **2A**, **3AA**, or **4AA** are included. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0601697

---

(24) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople. *Gaussian 98*, Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(25) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(26) Perdew, J. P.; Wang, Y. *Phys. Rev. B. Condens. Mater. Phys.* **1992**, *45*, 13244.

(27) The basis set was obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 9/12/01, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory, which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multiprogram laboratory operated by Battelle Memorial Institue for the U.S. Department of Energy under contract DE-AC06-76RLO 1830. Contact David Feller or Karen Schuchardt for further information.