Organometallics **2006,** *25,* 5113−5121

Synthesis of Dirhodium(II) Complexes with Several Cyclometalated Thienylphosphines

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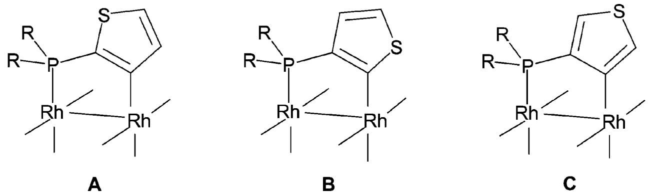
Received June 9, 2006

The thermal reaction of dirhodium tetraacetate with tris(3-thienyl)phosphine (**3TP**), diphenyl(3-thienyl)phosphine (**3TPPh$_2$**), and diphenyl(2-thienyl)phosphine (**2TPPh$_2$**) gives rise to mono-cyclometalated and bis-cyclometalated compounds; the latter can have a head-to-head (H−H) or head-to-tail (H−T) configuration. Bis-cyclometalated compounds with H−T configuration can be prepared in high yield under photochemical conditions or by combining irradiation with subsequent thermal treatment in acetic acid. The reactivity order of aromatic ring C−H activation is phenyl < 2-thienyl ≪ 3-thienyl, which leads to a selective activation of the thienyl ring. Thus, only one mono-cyclometalated compound is obtained from the thermal reaction with **3TPPh$_2$**, and activation of the thienyl ring competes favorably with activation at the phenyl rings in the case of **2TPPh$_2$**. The reaction of these mono-cyclometalated compounds with d_4-acetic acid was monitored by ^{1}H NMR spectroscopy, which demonstrates that the H/D exchange occurs during the demetalation step. The energy values calculated (DFT) for the different compounds agree with the experimental results.

Introduction

We have recently reported that the reaction of dirhodium tetraacetate with tris(2-thienyl)phosphine[1,2] yields dirhodium(II) compounds with the $Rh_2(O_2CCH_3)_{4-x}(PC)_x \cdot (CH_3CO_2H)_2$ general formula, which results from substituting one or two acetates for formal thienylphosphine anions that act as P,C bridging ligands. In this particular cyclometalation reaction, tris(2-thienyl)phosphine shows higher reactivity than triarylphosphines,[3−7] especially when the reaction is photochemically activated. Interestingly, the metalated rings of these compounds undergo a selective rearrangement of structure, from type **A** to type **B**, when treated with acetic acid (Scheme 1). However, the nonmetalated rings retain their original structure.

Scheme 1. Schematic Drawing of the Thienyl Ring Arrangement



Density functional theoretical (DFT) calculations[2] indicated that the rearrangement of one metalated thienyl ring from structure type **A** to structure type **B** lowered the energy of the compound by ca. 15 kJ/mol. In the case of bis-cyclometalated compounds with H−H or H−T configuration, such rearrangement provides products in which both metalated rings had structure **B**, with ca. 30 kJ/mol more stability than the corresponding products with structure type **A**. Under thermal conditions, the H−H compounds transform into their H−T isomers, which agrees with their calculated relative energy values.

We are now interested in extending these studies to other heteroaromatic phosphines, some of them chosen with a mixed set of aromatic substituents, to provide information about the relative rate of C−H activation of the aromatic rings. This report describes the synthesis and characterization of several dirhodium(II) compounds containing cyclometalated phosphines, such as tris(3-thienyl)phosphine (**3TP**), diphenyl(3-thienyl)phosphine (**3TPPh$_2$**), and diphenyl(2-thienyl)phosphine (**2TPPh$_2$**) (see Scheme 2). The compound labeling includes one or two letters that refer to the structure of the metalated ring(s) in mono- and bis-cyclometalated compounds, respectively. The energy values for the dirhodium compounds were calculated by DFT methods, and labeling experiments with deuterated acetic acid were used to explore the reactivity of the mono-cyclometalated compounds.

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10.1021/om0605128 CCC: $33.50

Results

Reactions of Dirhodium(II) Tetraacetate with Tris(3-thienyl)phosphine (3TP). The $Rh_2(O_2CCH_3)_3[(3\text{-}C_4H_2S)P[(3\text{-}C_4H_3S)_2]$ mono-cyclometalated compound (**1B** in Scheme 2) was obtained as the main product from the thermal reaction of dirhodium(II) tetraacetate with **3TP** (1:0.9 molar ratio) in refluxing (3:1) toluene/glacial acetic acid solution (Scheme 3a). Two bis-cyclometalated products with $Rh_2(O_2CCH_3)_2[(3\text{-}C_4H_2S)P(3\text{-}C_4H_3S)_2]_2$ formula, presenting metalated phosphines in a H−T (**2BB**) or H−H (**3BB**) configuration (Schemes 2 and 3a), were obtained when a 1:2 molar ratio of dirhodium tetraacetate to phosphine was used. Multinuclear NMR spectroscopy confirmed that the metalated ring had structure type **B** in each of the three compounds.

By contrast, irradiation (mercury lamp, Pyrex filter) of a solution of dirhodium(II) tetraacetate and **3TP** (1:2 molar ratio) in (9:1) CH_2Cl_2/acetic acid solution led to a ca. 1:1 mixture of two different H−T bis-cyclometalated products (Schemes 2 and 3a). A similar product distribution was detected when the photochemical reaction was performed at −30 °C. According to the ^{31}P NMR spectrum of the reaction crude, one of the compounds was identified as **2BB**, while the second compound had two different phosphorus environments. After separation of both compounds by chromatography, multinuclear NMR spectroscopy confirmed that in the second compound one metalated thienyl ring presented structure **B**, while the other had structure **C**, which agrees with its assignment as **2BC**. Interestingly, complete rearrangement from **2BC** to **2BB** was observed after heating a mixture of both compounds in acetic acid at 90 °C for 15 h (Scheme 3a). Therefore, the combination of photochemical and thermal treatments can be used to obtain thermodynamic product **2BB** in high yield and within a reasonable time scale. All attempts to crystallize these bis-cyclometalated compounds failed.

Reactions of Dirhodium(II) Tetraacetate with Diphenyl-(3-thienyl)phosphine (3TPPh$_2$). The reaction of dirhodium-(II) tetraacetate with **3TPPh**$_2$ (1:0.9 molar ratio) in a refluxing (9:1) toluene/acetic acid mixture gave mono-cyclometalated compound $Rh_2(O_2CCH_3)_3[(3\text{-}C_4H_2S)PPh_2]$ (**4B**) in 75% yield (Schemes 2 and 3b). In addition, bis-cyclometalated products with $Rh_2(O_2CCH_3)_2[(3\text{-}C_4H_2S)PPh_2]_2$ formula, presenting the metalated phosphines in a H−T (**5BB**) and H−H (**6BB**) configuration, were detected by ^{31}P NMR spectroscopy of the reaction mixture, although they were formed in low yield (<10%). However, these bis-cyclometalated compounds were obtained in higher yield and as a 1:1 mixture when 2 equiv of phosphine was used. Multinuclear NMR studies on the isolated products confirmed metalation of phosphines had occurred through the thienyl ring 3-position (structure type **B**).

Interestingly, the photochemical reaction gave results very similar to those already described for **3TP**. Thus, a mixture of two H−T compounds, in approximately equal amount, was obtained. One compound was identified as **5BB**, while the second, showing two different ^{31}P NMR resonances, was assigned as **5BC** (Schemes 2 and 3b). Isomerization from **5BC** to **5BB** was observed after heating the mixture of products at 90 °C in pure acetic acid. All the efforts to obtain single crystals from pure solutions of **5BB** failed, but they were accidentally obtained from a solution containing a mixture of **5BB** and **5BC**.

Reactions of Dirhodium(II) Tetraacetate with Diphenyl-(2-thienyl)phosphine (2TPPh$_2$). The reaction of dirhodium-(II) tetraacetate with **2TPPh$_2$** (1:0.9 molar ratio) in a refluxing (9:1) toluene/acetic mixture gave two mono-cyclometalated compounds in ca. 9:1 ratio (Schemes 2 and 3c). The major compound was isolated by chromatographic methods and identified by ^1H, ^{31}P, COSY, and HMBC NMR spectra as the compound with $Rh_2(O_2CCH_3)_3[(2\text{-}C_4H_2S)PPh_2]$ formula (**7A**), resulting from metalation through the thienyl ring (Figures S5 and S6 in SI). X-ray analysis of well-grown crystals from this compound agreed with this assignment. The minor compound was formulated as $Rh_2(O_2CCH_3)_3[(C_6H_4)P[(2\text{-}C_4H_3S)Ph]$ (**8**), which presented metalation at one of the phosphine phenyl rings.

By contrast, $Rh_2(O_2CCH_3)_2[(2\text{-}C_4H_2S)PPh_2]_2$ H−T bis-cyclometalated compound (**9AA**) was obtained in 70% yield upon irradiation of a mixture of dirhodium tetraacetate in the presence of 2 equiv of **2TPPh**$_2$ (Schemes 2 and 3c). Its structure was assigned on the basis of COSY and HMBC $^{31}P-^1H$ NMR spectra. Single crystals of $Rh_2(O_2CCF_3)_2[(2\text{-}C_4H_2S)PPh_2]_2\cdot(py)_2$ [**10AA·(py)2**] suitable for X-ray diffraction were obtained after replacing the acetate groups by trifluoroacetates and using pyridine as axial ligand (Scheme 2). They presented some disorder in one of the metalated thienyl rings, but the analysis confirmed the core structure assigned for **9AA**.

No evidence of reorganization of the metalated thienyl ring from type **A** to type **B** structure was observed in acetic acid media (Scheme 3c). This result contrasts with that found for the tris(2-thienyl)phosphine derivative.[2]

Again, though compound **9AA** was selectively obtained by photochemical methods, the thermal reaction of dirhodium(II) tetraacetate with **2TPPh$_2$** afforded a mixture of **9AA** and the H−H bis-cyclometalated product **11AA** (ca. 20%). This species was isolated as an adduct with water and pyridine molecules (**11AA·py·(H$_2$O)$_{0.5}$**), crystallized, and structurally characterized.

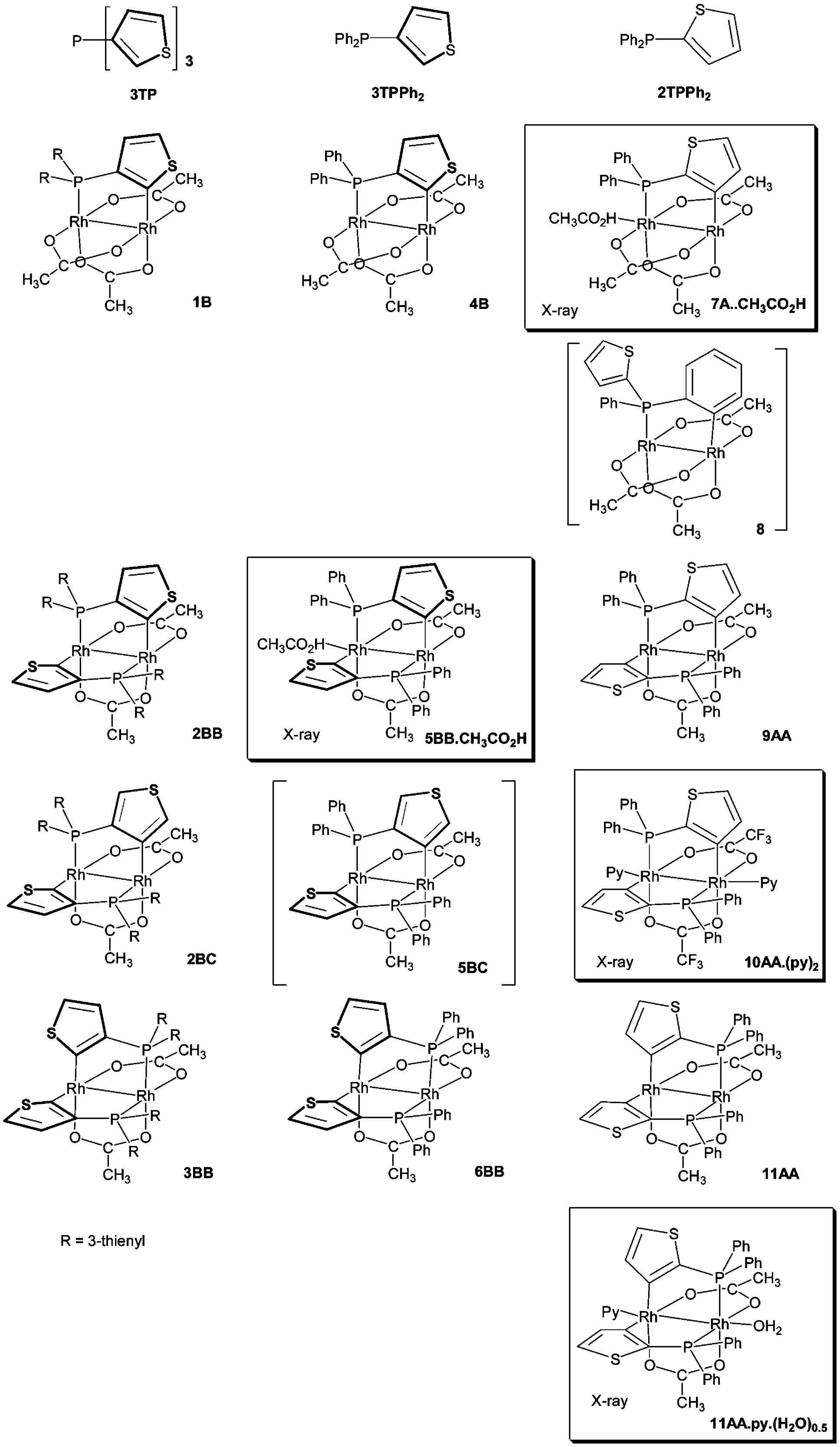
Solid State Structures. Complexes **5BB·CH$_3$CO$_2$H**, **7A·CH$_3$CO$_2$H**, **10AA·(py)$_2$**, and **11AA·py·(H$_2$O)$_{0.5}$** were investigated by X-ray crystallography in order to corroborate the spectroscopic findings. The molecular structures of all these compounds together with selected atom distances and bond angles are depicted in Figures S1−S4 (see SI). The Rh−Rh bond distances are in the range 2.4361(12) to 2.5980(6) Å, the mono-cyclometalated compounds showing shorter values than the bis-cyclometalated compounds. The replacement of acetic acid by pyridine as axial ligand increases the Rh−Rh bond distance.

The thienyl ring is essentially flat in all cases, and the C−C bond distances within the ring retain the short−long−short sequence with average values of 1.35, 1.42, and 1.35 Å. The Rh−P and Rh−C bond distances are very similar for the mono- and bis-cyclometalated compounds, with values in the range 2.21−2.23 and 1.98−2.01 Å, respectively, and the longest ones correspond to the H−H bis-cyclometalated compound **11AA·py·(H$_2$O)$_{0.5}$**. The Rh−O distances *trans* to P are slightly shorter than *trans* to C, this difference being more significant for **11AA·py·(H$_2$O)$_{0.5}$** (0.07 Å).

The structures for compounds **7A·CH$_3$CO$_2$H** and **11AA·py·(H$_2$O)$_{0.5}$** are as anticipated, not only in the ligand configuration but also in the structure of the metalated thienyl rings. The location of the sulfur atom in the metalated rings was established without ambiguity in all the compounds. In **5BB·CH$_3$CO$_2$H**, whose crystals accidentally grew from a mixture of isomers, detailed refinement confirmed some disorder in the metalated rings, with the sulfur atoms in the 3- and 4-positions. The best refinement was obtained for an 85% of occupation in the 3-position. Compound **10AA·(py)$_2$** also shows some disorder in one of the metalated rings, with the sulfur atom in the 2- and 3-position (Figure S3).

Compound **5BB·CH$_3$CO$_2$H** (Figure S1) contains in the lattice one molecule of acetic acid per mole of rhodium dimer. All

Scheme 2. Mono- and Bis-cyclometalated Compounds Obtained from 3TP, $3TPPh_2$, and $2TPPPh_2$[a]

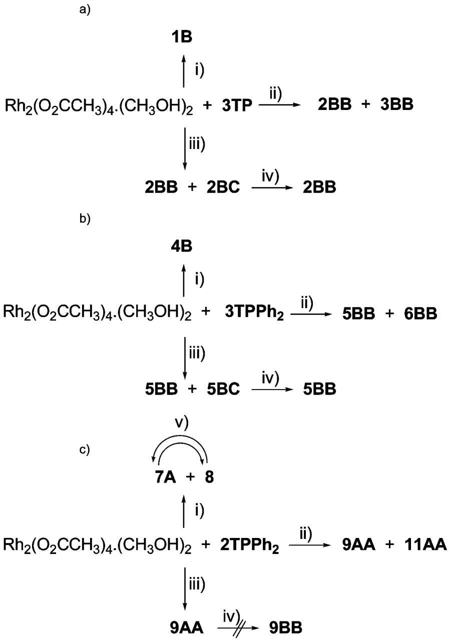


[a] Structures in frames are determined by X-ray. Compounds between brackets have been spectroscopically detected.

the distances indicate that the lattice molecule of acetic acid is establishing a hydrogen bond interaction with an oxygen atom of one bridging carboxylate ligand, with an O6···O1 distance of 2.7 Å. Compound **$7A{\cdot}CH_3CO_2H$** (Figure S2) also has one molecule of acetic acid in the lattice per rhodium dimer, but in this case no other interaction with the dirhodium molecule was found. Instead, two of these molecules are associated, forming dimers stabilized by hydrogen bonds.

Finally, in compound **$11AA{\cdot}py{\cdot}(H_2O)_{0.5}$** (Figure S4), there is one molecule of water showing symmetric hydrogen bond

Scheme 3. Thermal and Photochemical Reactions between $Rh_2(O_2CCH_3)_4.(CH_3OH)_2$ and 3TP (a), $3TPPh_2$ (b), and $2TPPh_2$ (c)



i) 1:0.9 molar ratio of $Rh_2(O_2CCH_3)_4.(CH_3OH)_2$ /phosphine, toluene/acetic acid, reflux
ii) 1:2 molar ratio o f$Rh_2(O_2CCH_3)_4.(CH_3OH)_2$ /phosphine, toluene/acetic acid, reflux
iii) hν, 1:2 molar ratio of $Rh_2(O_2CCH_3)_4.(CH_3OH)_2$ /phosphine, CH_2Cl_2/acetic acid
iv) acetic acid, 90 ºC
v) acetic acid, 70 ºC

interactions with two rhodium dimers, in particular with two O atoms of two carboxylate groups (O5···O1 distance of 2.73 Å).

Treatment of Mono-cyclometalated Compounds with Acetic Acid. As part of the comparative studies of reactivity for these compounds, we treated compounds **1B**, **4B**, and **7A** with d_4-acetic acid at 70 °C. The chemical evolution was followed by ^{1}H NMR spectroscopy.

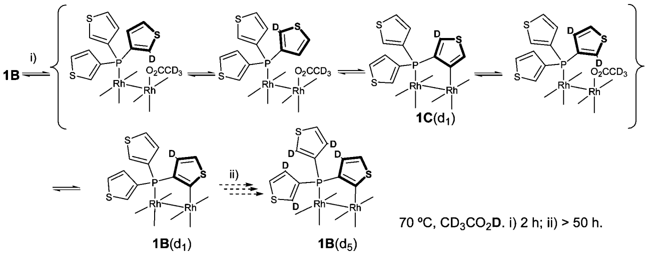
Compound 1B. Complete and selective H/D exchange was observed at the C-4 of the cyclometataled ring after 2 h, and compound **1B(d$_1$)** was selectively formed (Scheme 4). This exchange can be explained by rhodium–carbon bond cleavage following ring protonation/deuteration at the metalated position.

Such a process is relatively fast and selective, as no activation of the other thienyl rings was observed. Under these conditions, the introduction of deuterium at the nonmetalated thienyl rings required considerably longer reaction time (>50 h). This observation could indicate that rotation around the Rh–P bond is considerably slower than around the P–C bond. Only species **1B**, with different levels of H/D exchange, were spectroscopically observed in solution during all the process. The isomeric compound with structure **C** was not detected, in good agreement with the lower stability calculated for species with structure **C** (see below calculated data for **3TP-C**).

Compound 4B. Only H/D exchange at the metalated thienyl ring was detected when compound **4B** was treated under the same conditions as **1B**. No evidence of incorporation of deuterium into the phenyl rings or formation of isomeric species metalated through the phenyl rings was observed.

Compound 7A. Partial isomerization of compound **7A** to **8** (up to 78:22 ratio of **7A**/**8**) was observed when **7A** was dissolved in acetic acid and heated at 70 °C, reaching equilibrium after 10 h (point 2 in Figure S11). No changes were detected after extending the heating for 10 additional hours (point 3 in Figure S11). The solvent of this sample was removed under vacuum, and the solid residue was dissolved in CD_3CO_2D and heated at 70 °C for 12 h, leading to a ca. 50:50 ratio of **7A**/**8** (point 4 in Figure S11). However, after longer reaction time the **7A**/**8** molar ratio increased, reaching a 76:26 value after 135 h (point 5 in Figure S11), similar to the equilibrium mixture upon treatment in acetic acid. For comparison, **7A** led to a 55:45 molar ratio of **7A**/**8** when heated at 70 °C in d_4-acetic acid (point 1 in Figure S11). These observations can be attributed to isotopic effects (see below).

Scheme 4. H/D Exchange by Thermal Treatment of 1B in d_4-Acetic Acid



70 ºC, CD_3CO_2D. i) 2 h; ii) > 50 h.

The isomerization mixtures were analyzed by ^{1}H NMR, taking into account the signals belonging to **7A**, which had been previously isolated, and assigning the additional resonances to **8** (Figures S5–S10). From the analysis of the evolution from **7A** to **8** in d_4-acetic acid, it can be concluded that complete H/D exchange occurred at the thienyl ring C-3 of **8** (Figure S10 in SI). However, the H/D exchange at the phenyl ring *ortho*-position of both compounds increased from only about 30% after 12 h to 80% after 135 h of heating.

No evidence of reorganization of the metalated thienyl ring from type **A** to type **B** structure was observed in these experiments. This result contrasts with that found for the tris(2-thienyl)phosphine derivative.[2]

Computational Results. Theoretical (DFT) calculations were performed in order to clarify the reactivity of the thienylphosphines and the stability of the corresponding rhodium complexes.

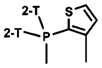
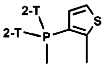
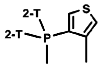
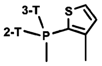
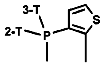
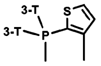
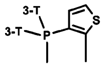
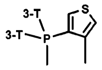
As a preliminary approach, the energy of **2TP** and **3TP**, as well as the phosphines containing a mixed set of thienyl substituents, **2,2,3TP** and **2,3,3TP**, were calculated. No significant differences were observed in the values for these four ligands (**2TP**: 0.0 kJ/mol, **2,2,3TP**: −1.3 kJ/mol, **2,3,3TP**: 0.5 kJ/mol, and **3TP**: 3.0 kJ/mol).

The energy values for the mono-cyclometalated dirhodium(II) compounds with symmetrical thienyl phosphines, **2TP** and **3TP**, as well as with the phosphines having a mixed set of thienyl substituents were also calculated (Table 1).

We observed that metalated compounds with structure type **B** are the least energetic. Thus, compound **1B** is found 23.7 kJ/mol more stable than the related compound **3TP-C**, whose metalated ring has structure **C**. In agreement with that, the latter isomer was not detected in any of the metalation reactions performed with **3TP**.

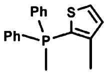
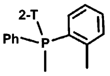
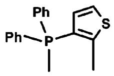
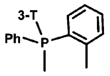
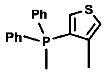
We have recently reported that mono-cyclometalated compounds derived from **2TP** undergo selective rearrangement of the metalated ring in the presence of acetic acid and adopt structure **B**.[2] This unusual ring rearrangement from structure type **A** to **B** is driven by the higher stability (15.8 kJ/mol) of the resulting species (see data for **2TP-B** and **2TP-A** in Table 1). On the other hand, substitution of 2-thienyl by 3-thienyl groups in the nonmetalated substituents of the phosphine also yields more stable mono-cyclometalated compounds, though the effect is relatively small (compare data for **3TP-B** with those for **2,3TP-B** and **2TP-B** in Table 1).

Table 1. Calculated Energy Values (kJ/mol) for $Rh_2(O_2CCH_3)_3(PC)\cdot(H_2O)_2$ Mono-cyclometalated Compounds with Tris-thienylphosphines as Ligands

PC	E E_{zp} $\Delta G_{(298)}$	PC	E E_{zp} $\Delta G_{(298)}$	PC	E E_{zp} $\Delta G_{(298)}$
 **2TP-A**[a]	0.0 0.0 0.0	 **2TP-B**[a]	-15.8 -15.8 -20.1	 **2TP-C**	8.7 8.3 3.4
 **2,3TP-A**	-2.1 -2.0 -7.1	 **2,3TP-B**	-17.1 -17.6 -23.0		
 **3TP-A**	-8.5 -7.8 -9.2	 **3TP-B (1B)**	-21.7 -21.9 -26.1	 **3TP-C**	2.0 1.4 1.4

[a] In ref 2.

Table 2. Calculated Energy Values (kJ/mol) for $Rh_2(O_2CCH_3)_3(PC)\cdot(H_2O)_2$ Mono-cyclometalated Compounds with Diphenylthienylphosphines as Ligands

PC	E E_{zp} $\Delta G_{(298)}$	PC	E E_{zp} $\Delta G_{(298)}$
 **Ph_2TP-A (7A)**	0.0 0.0 0.0	 **Ph,2TP-Ph (8)**	10.6 8.9 11.7
 **Ph_2TP-B (4B)**	-14.6 -15.3 -11.6	 **Ph,3TP-Ph**	9.5 8.3 15.9
 **Ph_2TP-C**	8.9 8.7 9.5		

The calculated energy values for the mono-cylometalated compounds with diphenylthienylphosphine ligands are shown in Table 2. In a qualitative sense, there is agreement between the experimental results for the isolated compounds and their calculated energies in the gas phase. Compound **7A** is only 10.6 kJ/mol more stable than **8**. We observed that the thermal reaction of dirhodium tetraacetate with **$2TPPh_2$** gave a mixture of both compounds, though **7A** was the major product. However, no mono-cyclometalated compound metalated at one phenyl ring was detected when using **$3TPPh_2$**, in good agreement with the higher stability of **4B** than **Ph,3TP-Ph** (ca. 25 kJ/mol). The same applies to the compound metalated through the 3-thienyl ring and with structure type **C** (**Ph_2TP-C**), which was not detected in solution, in good agreement with the higher stability of **4B** (ca. 24 kJ/mol).

Table 3. Calculated Energy (kJ/mol) for $Rh_2(O_2CCH_3)_2(PC)_2\cdot(H_2O)_2$ Bis-cyclometalated Compounds with Tris-thienylphosphines as Ligands

configuration		E $\Delta G_{(323)}$		E $\Delta G_{(298)}$
HT	**2TP-AA**[a]	0.0 0.0	**3TP-CC**	0.0 0.0
	2TP-AB[a]	−16.9	**3TP-BC** (**2BC**)	−23.2 −21.9
	2TP-BB[a]	−32.6 −29.6	**3TP-BB** (**2BB**)	−46.2 −45.2
HH	**2TP-AA**	25.0 27.7	**3TP-BB** (**3BB**)	−29.5 −21.4

[a] In ref 2.

Interestingly, in contrast with the case of the tris(2-thienyl)-phosphine mono-cyclometalated compound,[2] no rearrangement from structure **A** to **B** was observed upon thermal treatment of **7A** in acid media, despite the higher stability (ca. 15 kJ/mol) of **4B** compared to **Ph_2TP-A**.

Similar trends are observed for the energies of the bis-cyclometalated derivatives. Compounds with metalated 3-thienyl rings and with structure type **B** are energetically favored compared to other structures (Table 3).

Although calculations indicated that H−T bis-cyclometalated compounds with thienyl phosphines are more stable than the H−H isomers, both types of compounds formed from the thermal reactions of dirhodium tetraacetate and thienyl phosphines. Slow isomerization from H−H to H−T structure upon prolonged heating in acetic acid has been observed only for compounds derived from **2TP**.[2]

Discussion

In general, the thienylphosphines show higher reactivity than the aryl phosphines previously described. This increasing reactivity is especially remarkable under photochemical conditions; the thienyl phosphines readily yield the bis-cyclometalated compounds under conditions where the aryl phosphines only give mixtures of metalated compounds.[8] One additional detail is the higher tendency of the thienyl phosphines to form, under thermal conditions, bis-cyclometalated compounds with H−H arrangement of the phosphines. Fortunately, the H−T compounds can be selectively obtained, in moderate to high yield, when the reactions are performed under photochemical conditions. The DFT calculations confirm that bis-cyclometalated compounds with H−H structure have much higher energy value than the corresponding H−T isomers.

An interesting observation is the affinity of the rhodium atoms to sulfur atoms. Thus, in the absence of other donor molecules, some sort of aggregation is observed by NMR for the H−H product **3BB**. In these conditions, the two phosphorus atoms become nonequivalent. The addition of acetic acid produces again a symmetrical spectrum, and this is a reversible process. These observations suggest that an intermolecular interaction between the rhodium center of one molecule and a sulfur atom belonging to a thienyl group of other one occurs. All the efforts to obtain single crystals of **3BB** to confirm this association have failed.

The reactivity order of aromatic ring C−H activation (phenyl < 2-thienyl ≪ 3-thienyl) is in agreement with the relative energy values calculated for the dirhodium derivatives. Thus, only one mono-cyclometalated compound, **4B**, is obtained from the

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(8) Unpublished results.

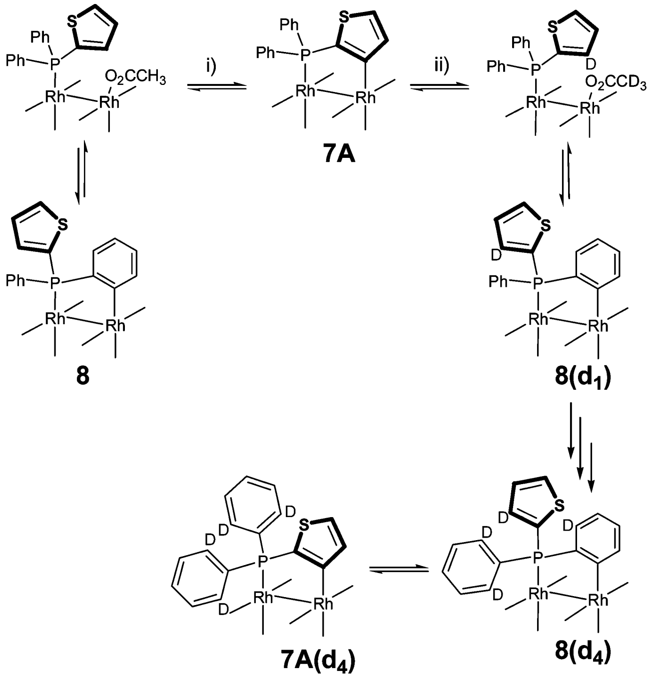
reaction of **3TPPh$_2$**, and two mono-cyclometalated compounds, **7A** and **8**, are obtained in a 9:1 ratio from the reaction with **2TPPh$_2$**.

For **3TP** and **3TPPh$_2$**, two carbon atoms from the 3-thienyl ring are accessible for C−H activation, giving rise to two types of structure, **B** or **C**. Calculations assign lower energy for the first type of structure, and in agreement with that, only compounds with two metalated ligands having structure **B**, **2BB** and **5BB**, can be obtained by a combination of photochemical and thermal reactions. Thus, irradiation of **3TP** with dirhodium tetraacetate gives a mixture of two products, the more stable **2BB** and the intermediate **2BC**. By thermal treatment, this intermediate rearranged to give **2BB** as the only product. The same applies to the reaction with **3TPPh$_2$**. A mixture of **5BB** and **5BC** is formed after irradiation, and again rearrangement of **5BC** to **5BB** is observed by thermal treatment of that mixture. However, if these reactions are thermally performed, mixtures of H−T (**2BB** and **5BB**) and H−H compounds (**3BB** and **6BB**) are obtained. In these cases, rearrangement from a H−H to a H−T structure is not detected, although such a process, according to the calculations, should be thermodynamically favored.

The treatment of mono-cyclometalated compounds with CD_3CO_2D provides interesting information on different processes occurring in solution. Evidence of reversible Rh−C bond cleavage and C−H bond activation is obtained in all the cases, but a detailed analysis was possible only for the more simple compounds, the mono-cyclometalated ones. In the case of compound **1B**, results indicate that all the processes yielding **1B(d$_1$)**, shown in Scheme 4, must be considerably faster than the rotation around the Rh−P bond, which would extend the H/D exchange to all the thienyl rings. Therefore, it is not surprising that complete and selective H/D exchange is obtained at the metalated thienyl ring for compound **4B**. The higher reactivity of the 3-thienyl rings toward the metalation reaction, compared to the phenyl rings, and the restricted rotation around the Rh−P bond prevent the incorporation of deuterium into the phenyl rings.

The selective deuteration at the C-4 position of the metalated thienyl ring in **1B** and **4B** can be easily explained. These two compounds undergo Rh−C bond cleavage when heated in acetic acid to form species with one equatorial ligand, **3TP** or **3TPPh$_2$**, respectively. Such species, which are considered intermediates in the metalation reaction, can undergo cyclometalation reaction via activation of any of the two available C−H bonds in the 3-thienyl ring, yielding finally metalated rings with structure **B** or **C**. The observation of deuterium incorporation at the C-4 position of the thienyl ring confirms that metalation takes places at both C-2 and C-4 carbon atoms. The fact that the mono-cyclometalated compound with structure type **C** is not observed in solution is in agreement with the lower stability calculated for this type of coordination, compared to structure type **B**. Additionally, it has been observed that bis-cyclometalated compounds having a metalated thienyl ring with structure type **C**, for example **2BC** or **5BC**, thermally rearrange to form the isomeric compounds with structure type **BB**.

Scheme 5. Evolution from 7A to 8 in (i) Acetic Acid and (ii) d$_4$-Acetic Acid



i) CH_3CO_2H; ii) CD_3CO_2D

The observed isomerization from **7A** to **8**, when the first compound is reacted with acid, is an additional evidence of activation of phenyl rings in **2TPPh$_2$**. In all the conditions used, compound **7A** is always the major product in this equilibrium. Calculations indicate that for phosphines with a mixed set of substituents, such as **2TPPh$_2$**, metalation at the thienyl ring yields a more stable isomer (**7A**) than metalation at the phenyl ring (**8**). The results after treatment of **7A** in acetic acid are in agreement with these calculations, as the **7A**:**8** molar ratio is ca. 3:1 at equilibrium, demonstrating that C−H activation at the thienyl ring is favored compared to the C−H activation at phenyls.

However, the fact that the final product distribution is different for acetic acid and d$_4$-acetic acid requires some comments. Assuming that the slowest process is the Rh−C bond cleavage and that differences in acid strength would produce only differences in the time required to reach the equilibrium, we propose that the higher **7A**/**8** is due to an isotopic effect.

Treatment of **7A** in d$_4$-acetic acid after 12 h yields a **7A**:**8** ratio of ca. 50:50. In this case, the formation of **7A** from the intermediate species requires C−D activation, while formation of **8** involves C−H activation. Therefore, the higher strength of the C−D bond compared to the C−H bond makes metalation at the phenyl ring more competitive and justifies the result. However, after longer reaction times, both phenyl groups become deuterated and, consequently, the molar ratio of products slowly evolves to the 3:1 initial value.

Conclusions

The thermal reaction of dirhodium tetraacetate with tris-(3-thienyl)phosphine (**3TP**), diphenyl(3-thienyl)phosphine (**3TPPh$_2$**), and diphenyl(2-thienyl)phosphine (**2TPPh$_2$**) gives rise to mono-cyclometalated compounds or bis-cyclometalated compounds (with head-to-tail (H−T) and head-to-head (H−H) configuration) depending on the $Rh_2(O_2CCH_3)_4$/phosphine molar ratio. The reactivity order of aromatic ring C−H activation is phenyl < 2-thienyl ≪ 3-thienyl, which leads to a selective activation of the thienyl ring. Bis-cyclometalated compounds, with symmetric H−T configuration, can be prepared in 63−77% yield under photochemical conditions or upon combination of photochemical and thermal treatment in acetic acid.

The available results confirm that the structure of type **B** is the most stable one for the metalated thienyl ligands. Under photochemical conditions, species with metalated thienyl moieties having structure type **C** have been detected as intermediates. Rearrangement from structure type **C** to type **B** takes place under thermal treatment. Additionally, the formation in acid media of intermediate species with structure type **C**, not spectroscopically detected, from complex **1B** or **4B** must be invoked in order to explain the observed incorporation of deuterium at the C-4 of the metalated ring in isotopic labeling experiments performed at 70 °C.

When Ph and 3-thienyl moieties are competing, **3TPPh$_2$**, selective activation of the thienyl ring is always observed. These results are in good agreement with the difference in the energy values ($\Delta G°$ 27 kJ/mol) calculated for the corresponding compounds resulting from activation (Table 2). However, competition of Ph and 2-thienyl rings gives a mixture of compounds resulting from activation of the 2-thienyl (**7A**) and phenyl rings (**8**). The equilibrium between these two species was also studied in some detail.

Finally, the energy values calculated (DFT) for the different compounds are in good agreement with the experimental results.

Experimental Section

Computational Details. All calculations were carried out with the Gaussian98 program package.[9] The DFT level of theory with the nonlocal density functional B3PW91[10] was selected for the quantum chemical studies. The basis set comprised the Stuttgart–Dresden effective small core potential[11] 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.

General Comments. $Rh_2(O_2CCH_3)_4$·$(CH_3OH)_2$ was purchased from Pressure Chemical Co. $P(3\text{-}SC_4H_3)_3$, $P(3\text{-}SC_4H_3)Ph_2$, and $P(2\text{-}SC_4H_3)Ph_2$ were prepared by standard methods using nucleophilic displacement on PCl_3 or $PClPh_2$.[12]

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

Synthesis of $Rh_2(O_2CCH_3)_3[(3\text{-}C_4H_2S)P(3\text{-}C_4H_3S)_2]$ (1B). $Rh_2(O_2CCH_3)_4$·$(CH_3OH)_2$ (100 mg, 0.20 mmol) was dissolved in toluene/acetic acid (20 mL, 3:1), and **3TP** (50 mg, 0.18 mmol) was added. The color changed nearly immediately to purple, and the mixture was heated for 2 h under reflux. The solvent was evaporated under reduced pressure and the product purified by column chromatography using 100:20:0.5 toluene/AcOEt/AcOH mixtures. The desired product was collected from a dark gray band and obtained pure after evaporation of the solvents, crystallization from CH_2Cl_2/hexanes, and washing with Et_2O/hexanes. **1B** was obtained as a gray solid poorly soluble in the absence of acetic acid (yield 74 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.43 (s, *cis*-CH_3CO$_2$, 6H), 2.34 (s, *trans*-CH_3CO$_2$, 3H), 7.26 (dd, J = 5.1 Hz, J = 2.2 Hz, 1H), 7.33 (m, 2H), 7.48 (m, 3H), 7.63 (m, 2H). ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$, 298 K): δ 23.51 (s), 23.80 (s), 126.21 (d, J = 12.5 Hz), 128.03 (b), 130.25 (d, J = 14.1 Hz), 132.04 (d, J = 12.6 Hz), 146.62 (d, J = 55.4 Hz), 183.10 (s), 190.12 ppm (s). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$/acetic acid, 298 K): δ −5.23 ppm (bd, $^1J_{P,Rh}$ = 150 Hz). Anal. Calcd for **1B·$(CH_3CO_2H)_2$**, $C_{20}H_{21}O_8PRh_2S_3$ (722.4): C 33.25, H 2.93. Found: C 33.54, H 2.90.

Synthesis of (H–T) $Rh_2(O_2CCH_3)_2[(3\text{-}C_4H_2S)P(3\text{-}C_4H_3S)_2]_2$ (2BB). $Rh_2(O_2CCH_3)_4$·$(CH_3OH)_2$ (100 mg, 0.2 mmol) and 3TP (120 mg, 0.43 mmol) were dissolved in a mixture of CH_2Cl_2 and AcOH (100 mL, 9:1). The resulting solution was irradiated for 6 h. The solvent was evaporated under reduced pressure, and the residue, dissolved in acetic acid, was heated at 90 °C for 15 h. After evaporation of the solvent and filtration through silica (CH_2Cl_2/Et_2O, 9:1), **2BB** was crystallized as a violet solid (yield, 110 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.53 (s, 6H), 6.86 (m, 2H), 6.88 (m, 2H), 6.98 (m, 2H), 7.12 (m, 2H), 7.19 (m, 2H), 7.36 (m, 2H), 7.40 (m, 2H), 7.52 ppm (m, 2H). ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$, 298 K): δ 22.87 (s), 125.67 (d, J = 12.8 Hz), 126.82 (d, J = 12.4 Hz), 128.35 (d, J = 10.0 Hz), 129.70 (d, J = 10.7 Hz), 130.13 (d, J = 14.6 Hz), 130.72 (d, J = 7.8 Hz); 130.80 (d, J = 4 Hz), 182.16 ppm (s). ^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$, 298 K): δ −1.70 ppm (AA′XX′ system). Anal. Calcd for **2BB·$(H_2O)_2$**, $C_{28}H_{26}O_6P_2Rh_2S_6$ (918.7): C 36.60, H 2.85. Found: C 36.57, H 3.23.

Synthesis of (H–T) $Rh_2(O_2CCH_3)_2[(3\text{-}C_4H_2S)P(3\text{-}C_4H_3S)_2]$-$[(3'\text{-}C_4H_2S)P(3\text{-}C_4H_3S)_2]$ (2BC). $Rh_2(O_2CCH_3)_4$·$(CH_3OH)_2$ (100 mg, 0.2 mmol) and **3TP** (120 mg, 0.43 mmol) were dissolved in a mixture of CH_2Cl_2 and AcOH (100 mL, 9:1). The resulting solution was irradiated for 6 h. The solvent was evaporated under reduced pressure, and the residue was transferred to a chromatography column. First elution with a 80:20:0.5 toluene/AcOEt/AcOH mixture eliminated decomposition compounds and phosphine oxides. The remaining violet fraction was collected and was submitted to a second chromatography. Starting the elution with a 100:6:0.5 CH_2Cl_2/Et_2O/AcOH mixture and increasing polarity different fractions were collected and were analyzed by phosphorus NMR spectroscopy. The first fractions contained compound **2BB** (yield, 71 mg, 35%), while the last fractions that contained **2BC** were evaporated and the residue was crystallized from dichloromethane/hexanes/AcOH (yield, 60 mg, 29%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.28 (s, 3H), 1.56 (s, 3H), 6.75 (m, 1H), 6.86 (m, 2H), 6.88 (m, 1H), 7.00 (m, 1H), 7.14 (b, 1H), 7.21 (b, 1H), 7.43–7.36 (m, 3H), 7.55 ppm (m, 1H). ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$, 298 K): δ 22.60 (dd, J = 6.5 Hz, J = 2.6 Hz), 119.82 (d, 19.9 Hz), 132–124 (overlapping multiplets), 133.53 (d, J = 58.1 Hz), 133.91 (d, J = 27.2 Hz), 134.85 (d, J = 63.8 Hz), 137.94 (d, J = 76.4 Hz), 141.96 (d, J = 75.8 Hz), 145.42 (m), 167.48 (m,

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metalated), 181.95 (d, J = 2,1 Hz; CO_2), 182.45 ppm (d, J = 2.1 Hz, CO_2). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 298 K): δ 4.08 (dd, $^1J_{(P,Rh)}$ = 169.0 Hz, $^2J_{P,Rh}$ = 6.1 Hz), −0.4 ppm (dd, $^1J_{P,Rh}$ = 169.4 Hz, $^2J_{P,Rh}$ = 6.5 Hz). The solid products obtained by crystallization from solutions containing acetic acid did not provide reproducible elemental analysis.

Synthesis of (H−H) Rh_2 $(O_2CCH_3)_2[(3\text{-}C_4H_2S)P(3\text{-}C_4H_3S)_2]_2$ (3BB). $Rh_2(O_2CCH_3)_4{\cdot}(CH_3OH)_2$ (113 mg, 0.22 mmol) was dissolved in toluene/acetic acid (20 mL, 3:1). **3TP** (225 mg, 80 mmol) was added to the hot (ca. 100 °C) solution, which immediately changed to red-violet color. After refluxing for 3 h the solvent was evaporated and the residue was passed to a chromatography column, eluted using a 100:20:0.5 toluene/AcOEt/AcOH mixture. The main colored fraction was collected and evaporated, and the residue was transferred again to a chromatography column that was eluted using a 50:3 CH_2Cl_2/Et_2O mixture. A first fraction containing **3BB** was eluted followed by a second one, which contained compound **2BB**. From the first band, **3BB** was obtained as a red crystalline solid (yield, 47 mg, 21%). ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.30 (s, 3H, $C\mathit{H}_3CO_2$, *trans* to P_B), 1.91 (s, 3H, $C\mathit{H}_3CO_2$, 3H, *trans* to P_A), 6.03 (m, 1H, P_B), 6.26 (d, J = 4.83 Hz, 1H, P_B), 6.64 (m, 1H P_B), 6.69 (dd, J = 2.32 Hz, J = 5.2 Hz, 1H, P_B), 6.81 (m, 1H, P_A), 7.04 (d, J = 4.4 Hz, 1H, P_A), 7.14 (b, 1H, P_A), 7.20 (m, 1H, P_A), 7.25 (m, 1H, P_A), 7.32 (d, J = 5.0 Hz, 1H, P_B), 7.44 (m, 1H, P_B), 7.51 (m, 2H, $P_B + P_A$), 7.75 (d, J = 5.3 Hz, 1H, P_A), 7.92 ppm (d, J = 5.6 Hz, 1H, P_A) 8.18 (d, J = 5.0 Hz, 1H, P_B). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, 298 K): δ 22.41 (s, $\mathit{C}H_3CO_2$, *trans* to P_B), 24.40 (s,$\mathit{C}H_3CO_2$, *trans* to P_A), 123.3 (d, J = 12.0 Hz, P_B), 124.6−125.1 (overlapping multiplets), 125.82 (d, J = 11.5 Hz, P_A), 126.91 (d, J = 12.6 Hz, P_B), 129.04 (d, J = 10.5 Hz, P_B), 129.52 (d, J = 11.5 Hz, P_A), 130.0−132.4 (overlapping multiplets), 133.00 (d, J = 31.9 Hz), 133.74 (d, J = 14.1 Hz), 134.63 (d, J = 56.0 Hz), 136.68 (d, J = 51.7 Hz), 138.42 (d, J = 74.8 Hz), 139.27 (dd, J = 2.9 Hz; J = 74.0 Hz), 162.40 (dd, J = 35.6 Hz, J = 41.8 Hz, $RhCCP_B$), 173.11 (dd, J = 36.6 Hz; J = 43.9 Hz, $Rh\mathit{C}CP_A$), 181.82 (d, J = 2.6 Hz, *trans*-$CH_3\mathit{C}O_2$(equatorial), P_A), 181.90 ppm (d, J = 2.1 Hz, *trans*-$CH_3\mathit{C}O_2$(equatorial), P_B). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 298 K): δ 2.8 (ddd, $^1J_{P,Rh}$ = 150.7 Hz, $^2J_{P,P}$ = 43.5 Hz, $^2J_{P,Rh}$ = 5.8 Hz, P_A), −7.4 ppm (ddd, $^1J_{P,Rh}$ = 152.3 Hz, $^2J_{P,P}$ = 43.3 Hz, $^2J_{P,Rh}$ = 5.8 Hz, P_B). Anal. Calcd for **3BB·$(CH_3CO_2H)_2$**, $C_{32}H_{30}O_8P_2Rh_2S_6$ (1002.7): C 38.32, H 3.01. Found: C 38.65, H 3.10.

NMR data of **3BB** in $CDCl_3$ with traces of CH_3CO_2H mixtures: ^1H NMR (400 MHz, $CDCl_3/CH_3CO_2H$, 298 K): δ 1.60 (s, $C\mathit{H}_3CO_2$, 6H), 6.59 (d, J = 3.7 Hz, 2H), 6.84−6.81 (m, 4H), 6.95 (m, 2H), 7.11 (m, 2H), 7.20 (d, J = 5.2 Hz, 2H), 7.25 (m, 2H), 7.32 ppm (m, 2H). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, 298 K): δ 19.85 (s), 123.73 (m), 124.33 (m), 127.47 (m), 128.58 (m), 129.43 (m), 130.27 (m), 136.82 (m), 167.40 (m, metalated), 176.62 (s), 182.00 ppm (s). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3/CH_3CO_2H$, 298 K): δ −3.1 ppm (dd, $^1J_{P-Rh}$ = 152.9 Hz, $^2J_{P-Rh}$ = 7.2 Hz).

Synthesis of $Rh_2(O_2CCH_3)_3[(3\text{-}C_4H_2S)PPh_2]$ (4B). $Rh_2(O_2CCH_3)_4{\cdot}(CH_3OH)_2$ (100 mg, 0.2 mmol) and **3TPPh$_2$** (50 mg, 0.18 mmol) were dissolved in toluene/AcOH (50 mL, 9:1), giving a dark gray-purple solution, which was refluxed for 2 h, yielding a dark green-gray solution. After evaporation of the solvent under reduced pressure the residue was purified by column chromatography. Using a mixture of toluene/AcOEt/AcOH (100:20:0.5) a reddish fraction of double-metalated product came off. Then elution with a 60:20:0.5 toluene/AcOEt/AcOH mixture afforded a gray fraction, which after crystallization gave **4B** (yield, 94 mg, 75%). ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.38 (s, *cis*-$C\mathit{H}_3CO_2$, 6H), 2.35 (s, *trans*-$C\mathit{H}_3CO_2$, 3H), 7.13 (dd, J = 5 Hz, J = 2 Hz, 5-CH_2S, 1H), 7.31 (m, Ph, 4H), 7.38 (m, 2H), 7.45 (m, 1H), 7.61 ppm (m, 4H). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, 298 K): δ 19.50 (s), 20.81 (s), 127.70 (b), 127.97 (d, J = 10 Hz), 128.50 (bd, J = 8.4 Hz), 129.81 (d, J = 2.5 Hz), 132.5 (s), 132.83 (d, J = 53.0 Hz), 132.85 (d, J = 9.9 Hz), 134.56 (d, J = 72.0 Hz), 166.08 (m, metalated), 183.28 (s) 190.12 (s). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 298 K): δ 11.23 ppm (dd, $^1J_{P,Rh}$ = 148.5 Hz, $^2J_{P,Rh}$ = 4.7 Hz). Anal. Calcd for **4B·CH_3CO_2H**, $C_{24}H_{25}O_8PRh_2S$ (710.3): C 40.58, H 3.54. Found: C 40.57, H 3.65.

Synthesis of (H−T) $Rh_2(O_2CCH_3)_2[(3\text{-}C_4H_2S)PPh_2]_2$ (5BB). $Rh_2(O_2CCH_3)_4{\cdot}(CH_3OH)_2$ (150 mg, 0.3 mmol) and **3TPPh$_2$** (175 mg, 0.65 mmol) were dissolved in a mixture of CH_2Cl_2 and AcOH (100 mL, 9:1). The resulting solution was irradiated for 6 h, the solvent was evaporated under reduced pressure, and the residue, dissolved in acetic acid, was heated at 90 °C for 15 h. After evaporation of the solvent and filtration through silica (CH_2Cl_2/Et_2O, 9:1) compound **5BB** was crystallized as a violet solid (yield, 230 mg, 70%). ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.46 (s, 6H), 6.81 (dd, J = 5.1 Hz, J = 1.7 Hz, 2H), 7.08 (dd, J = 5.1 Hz, J = 1.2 Hz, 2H), 7.22 (m, 8H), 7.29 (m, 2H), 7.33 (m, 6H), 7.80 ppm (m, 4H). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, 298 K): δ 22.7 (d, J = 2.6 Hz), 126.3 (d, J = 11.6 Hz), 127.5 (d, J = 6.1 Hz), 127.6 (d, J = 5.8 Hz), 128.7 (d, J = 2.5 Hz), 129.1 (d, J = 2.3 Hz), 129.4 (d, J = 9.3 Hz), 132.0 (d, J = 9.1 Hz), 133.2 (d, J = 9.4 Hz), 133.8 (d, J = 53.8 Hz), 134.2 (d, J = 47.6 Hz), 135.2 (d, J = 77.0 Hz), 167.7 (m, metalated), 182.4 ppm (s). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 298 K): δ 10.6 ppm (AA′XX′ system). Anal. Calcd for **5BB·CH_3CO_2H**, $C_{38}H_{34}O_6P_2Rh_2S_2$ (918.6): C 49.68, H 3.73. Found: C 49.40, H 3.98.

Synthesis of (H−H) $Rh_2(O_2CCH_3)_2[(3\text{-}C_4H_2S)PPh_2]_2$ (6BB). $Rh_2(O_2CCH_3)_4{\cdot}(CH_3OH)_2$ (150 mg, 0.3 mmol) and **3TPPh$_2$** (175 mg, 0.65 mmol) were dissolved in a mixture of toluene/glacial acetic acid (100 mL, 90:10), and the solution was refluxed for 8 h. After evaporation, the residue was submitted to standard column chromatography, eluting with 100:10:0.5 CH_2Cl_2/Et_2O/AcOH. The first violet band collected contained compound **6BB** (yield, 55 mg, 19%) followed by a second violet band due to compound **5BB** (yield, 121 mg, 42%). ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.39 (s, 6H), 6.69 (m, 4H), 6.86 (m, 8H), 7.32 (m, 4H), 7.40 (m, 2H), 7.53 (d, J = 6.4 Hz, 2H), 7.73 (m, 4H). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, 298 K): δ 23.44 (s), 124.20 (s), 127.03 (m), 127.43 (m), 128.48 (s), 128.89 (s), 129.32 (s), 132.68 (m), 133.52 (m) 135.25 (s) 136.15 (s), 164.55 (m, metalated), 181.30 ppm (s). $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$, 298 K): δ 24.88 (dd, $^1J_{P-Rh}$ = 153.8 Hz, J = 5.0 Hz). The solid products obtained by crystallization from solutions containing acetic acid did not provide reproducible elemental analysis.

Synthesis of $Rh_2(O_2CCH_3)_3[(2\text{-}C_4H_2S)PPh_2]$ and $Rh_2(O_2CCH_3)_3[(C_6H_4)P(2\text{-}C_4H_2S)Ph]$ (7A and 8). 2TPPh$_2$ (60 mg, 0.22 mmol) and $Rh_2(O_2CCH_3)_4{\cdot}(CH_3OH)_2$ (118 mg, 0.23 mmol) were dissolved in a mixture of toluene/acetic acid (55 mL, 9:1), and the solution was heated under reflux for 3 h. After cooling, the solvent was evaporated under reduced pressure and the resulting brown solid was dissolved in CH_2Cl_2/AcOH (2 mL, 10:0.1), transferred to a chromatography column, and eluted with the same mixture of solvents. The eluted green-gray band was collected in two separate fractions. The first fraction was evaporated and the residue crystallized from CH_2Cl_2/hexanes/AcOH (5%), giving **7A** as a green-gray crystalline solid (yield, 72 mg, 50%). Single crystals of **7A** suitable for X-ray diffraction were obtained from the same mixture of solvents by slow evaporation. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.43 (s, 6H, *cis*-$C\mathit{H}_3CO_2$), 2.15 (s, 3H, *trans*-$C\mathit{H}_3CO_2$), 7.46 (m, 4H), 7.51 (m, 2H), 7.75 (m, 4H), 7.88 (dd, J = 5.0 Hz, J = 2.6 Hz, 1H), 8.05 ppm (dd, J = 4.8 Hz, J = 2.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, 298 K): δ 21.64 (s), 23.69 (s), 127.93 (d, J = 10.8 Hz), 128.51 (d, J = 3.2 Hz), 129.93 (d, J = 2.7 Hz), 132.86 (d, J = 10.3 Hz), 133.74 (s), 134.66 (dd, J = 18.1 Hz, J = 1.3 Hz), 164.91 (m), 179.44 (b), 182.74 (s), 182.77 (s). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 298 K): δ 14.74 ppm (dd, $^1J_{P-Rh}$ = 153.4 Hz, $^2J_{P-Rh}$ = 5.2 Hz). Anal. Calcd for **7A·**

CH_3CO_2H, $C_{24}H_{25}O_8PRh_2S$ (710.3): C 40.58, H 3.54. Found: C 40.34, H 3.73.

The second fraction contained a mixture of **7A** and **8** in a 4:1 ratio. Additional chromatographic enrichment provided solutions with a 1:1 ratio of both compounds that allowed the spectroscopic characterization of **8**. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.29 (s, 3H, *cis*-CH_3CO_2(equatorial)), 1.36 (s, 3H, *cis*-CH_3CO_2-(equatorial)), 2.36 (s, 3H, *cis*-CH_3CO_2(*trans*)), 6.98 (m, 1H), 7.10 (m, 2H), 7.26 (m, 1H), 7.32 (m, 2H), 7.38 (m, 1H), 7.43 (m, 1H), 7.54 (m, 2H), 7.65 (m, 1H), 8.62 ppm (m, 1H). ^{1}H NMR (400 MHz, CD_3CO_2D, 298 K): δ 6.98 (m, 1H), 7.11 (m, 1H), 7.17 (m, 1H), 7.27 (m, 1H), 7.36 (m, 2H), 7.43 (m, 1H), 7.50 (m, 1H), 7.57 (m, 2H), 7.73 (m, 1H), 8.48 ppm (m, 1H). ^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$, 298 K): δ 11.5 ppm (dd ^{1}J(P,Rh) = 151.8 Hz, ^{2}J(P,-Rh) = 6.2 Hz). The isolation of compound **8** in a pure state was not achieved. Additional spectroscopic data concerning its structural assignment are included in the SI.

Synthesis of H−T $Rh_2(O_2CCH_3)_2[(2\text{-}C_4H_2S)PPh_2]_2$ (9AA). $Rh_2(O_2CCH_3)_4{\cdot}(CH_3OH)_2$ (100 mg, 0.2 mmol) and **2TPPh$_2$** (120 mg, 0.44 mmol) were dissolved in a mixture of CH_2Cl_2/AcOH (100 mL, 9:1 ratio). The mixture was irradiated for 5−6 h, and the solvent was evaporated under reduced pressure. The resulting product was purified by standard column chromatography (SiO_2, hexanes/AcOEt (3:1 to 2:1 ratio)), giving **9AA** (yield 118 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.43 (s, 6H), 6.36 (dd, J = 6.4, J = 3.2 Hz, 2H), 7.14 (m, 8H), 7.19 (dd, J = 6.4, J = 2.4 Hz, 2H), 7.25 (m, 2H), 7.36 (m, 6H), 7.84 (m, 4H). ^{13}C{1H} NMR (100.5 MHz, $CDCl_3$, 298 K): δ 23.01 (d, J = 4 Hz), 127.29 (d, J = 13.8 Hz), 127.49 (d, J = 13.5 Hz); 128.83 (d, J = 3.5 Hz), 128.96 (s), 129.17 (d, J = 3.5 Hz), 132.28 (d, J = 12.6 Hz), 133.31 (d, J = 13.5 Hz), 134.99 (d, J = 23.6 Hz), 134.68 (d, J = 32.9 Hz), 134.96 (d, J = 22.6 Hz), 164.96 (m, metalated), 181.72 ppm (d, J = 2.3 Hz). ^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$, 298 K): δ 16.82 ppm (AA′XX′ system). Anal. Calcd for **9AA·($CH_3CO_2H)_2$**, $C_{40}H_{38}O_8P_2Rh_2S_2$ (978.7): C 49.09, H 3.91. Found: C 48.84, H 4.01.

Synthesis of H−T $Rh_2(O_2CCF_3)_2[(2\text{-}C_4H_2S)PPh_2]_2$ (10AA). To a solution of **9AA** (150 mg, 0.23 mmol) in chloroform (5 mL) was added CF_3CO_2H (0.1 mL). After 5 min stirring, the solvents were removed under vacuum at RT. This procedure was repeated five times. The resulting product was purified by column chromatography on SiO_2 with CH_2Cl_2/Et_2O (9:1 ratio). The collected fraction was concentrated and precipitated with hexanes as a violet powder. The solid was dissolved in dichloromethane (3 mL), and pyridine (0.1 mL) was added. Addition of hexanes and slow evaporation gave **10AA·(py)$_2$** (yield, 130 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 6.63 (m, 2H), 6.95 (m, 4H), 7.15 (m, 10H); 7.51 (m, 12H), 7.80 (m, 2H), 8.65 ppm (d, J = 8,7 Hz, 4H). ^{13}C-{^{1}H} NMR (100.5 MHz, $CDCl_3$, 298 K): δ 116.0 (q $^{1}J_{C-F}$ = 288 Hz), 124.4 (s, NCC), 127.8−126.7 (overlapping multiplets), 129.4 (s), 129.7 (s), 132.8−133.5 (overlapping multiplets), 133.6 (d, J = 21.4 Hz), 135.2 (d, J = 17.8 Hz), 137.1 (s), 151.7 (s, CN), 161.6 (m, metalated), 166.8 ppm (q, $^{2}J_{C-F}$ = 38 Hz). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$, 298 K): δ 15.09 ppm (dd, $^{1}J_{P-Rh}$ = 169.6 Hz, $^{2}J_{P-Rh}$ = 5.9 Hz). Anal. Calcd (%) for **10AA·(py)$_2$**, $C_{46}H_{34}F_6O_4P_2Rh_2S_2$ (1124.7): C 49.12, H 3.04. Found: C 48.92, H 3.08.

Slow evaporation of the solvents from a CH_2Cl_2/hexanes solution of the pyridine adduct afforded single crystals of **10AA·(py)$_2$**, suitable for X-ray diffraction.

Synthesis of H−H $Rh_2(O_2CCH_3)_2[(2\text{-}C_4H_2S)PPh_2]_2$ (11AA). To a well-stirred solution of $Rh_2(O_2CCH_3)_4{\cdot}(CH_3OH)_2$ (250 mg, 0.5 mmol) in toluene/AcOH (30 mL, 2:1) at 100 °C was slowly added **2TPPh$_2$** (295 mg, 1.1 mmol) in 10 mL toluene. After refluxing the mixture for 2.5 h the solvent was removed under reduced pressure. The residue was transferred to a chromatography column eluted with hexanes/AcOEt (2:1 to 1:3 ratio), separating two bands. The second violet fraction corresponds to the already described H−T compound **10AA** (198 mg, 41%). The first fraction, corresponding to **11AA**, was evaporated under reduced pressure, and the residue was precipitated with hexanes (yield, 75 mg, 17%). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$, 298 K): δ 18.5 ppm (dd, $^{1}J_{P-Rh}$ = 154.7 Hz, $^{2}J_{P-Rh}$ = 7.2 Hz). The solid was dissolved in dichloromethane, and three drops of pyridine were added. Addition of hexanes and slow evaporation gave single crystals of **11AA·py·(H$_2$O)$_{0.5}$**, suitable for X-ray diffraction. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.41 (s, 6H), 2.14 (s, 2H), 6.73 (m, 6H), 6.90 (m, 8H), 7.34 (m, 6H), 7.42 (m, 2H), 7.55 (d, J = 4.9 Hz, 2H), 7.76 (m, 2H), 7.86 (m, 1H), 8.94 ppm (m, 2H). ^{31}C{^{1}H} NMR (100.5 MHz, $CDCl_3$, 298 K): δ 21.95 (s), 23.17 (s), 125.32 (s), 127.05 (d, J = 5.4 Hz), 127.12 (d, J = 5.2 Hz), 127.38 (d, J = 5.2 Hz), 127.38 (d, J = 5.2 Hz), 127.45 (d, J = 5.2 Hz), 128.75 (d, J = 10.8 Hz), 128.90 (d, J = 10.8 Hz), 132.63 (d, J = 5.3 Hz), 132.70 (d, J = 5.3 Hz), 133.00 (d, J = 5.0 Hz), 133.07 (d, J = 5.0 Hz), 133.84 (d, J = 9.2 Hz), 133.96 (d, J = 9.4 Hz), 134.57 (s), 152.25 (s), 164.60 (m, metalated), 179.37 (b), 181.30 ppm (s). ^{31}P-{^{1}H} NMR (161.9 MHz, $CDCl_3$, 298 K): δ 22.61 ppm (dd, $^{1}J_{P-Rh}$ = 155.0 Hz, $^{2}J_{P-Rh}$ = 3.7 Hz). Anal. Calcd for **(11AA.py)$_2$·H$_2$O**, $C_{82}H_{72}N2O_9P_4Rh_4S_4$ (1893.3): C 52.02, H 3.83. Found: C 51.88, H 3.95.

Experiments of Chemical Evolution in Acid Media. In a standard experiment **7A** (5 mg, 6.5 × 10^{-3} mmol) was dissolved in acetic acid (0.45 mL), and the solution was monitored by ^{1}H and/or ^{31}P NMR spectroscopy at 70 °C, recording a new spectrum every 15 min.

Crystal structure data for **5BB·CH_3CO_2H**, **7A·CH_3CO_2H**, **2B**, **10AA·(py)$_2$**, and **11AA·py·(H$_2$O)$_{0.5}$** can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif.

Acknowledgment. Financial support by the Spanish Government (Project MAT2002-0442-1-C02-02 and J. Lloret fellowship) is gratefully acknowledged.

Supporting Information Available: COSY and HMBC ^{1}H−^{31}P spectra for compound **7A**, as well as spectra of the evolution from **7A** to **8** (^{31}P{^{1}H} and ^{1}H NMR and COSY spectra of **7A**/**8** mixtures) are included. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0605128