Synthesis, Structure, and Spectroscopy of (Thiapentadienyl)rhodium Phosphine Complexes[1]

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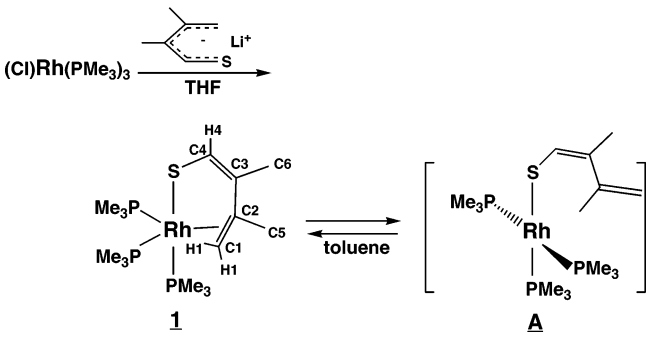
Summary: The reactions of (Cl)Rh(PR$_3$)$_3$ (R = Me, Et) with the anionic thiapentadienide reagent lithium 2,3-dimethyl-5-thiapentadienide have been investigated. In each case, the kinetic product exhibits a thiapentadienyl bonding mode in which the sulfur atom is σ-bonded to rhodium; however, ligand rearrangement yields thermodynamic isomers in which the carbon end of the thiapentadienyl chain is σ-bonded to rhodium.

During the past two decades, the chemistry of (pentadienyl)metal complexes has been extensively investigated.[2] Considerably less effort has been directed toward synthesizing and studying the reactivity of (heteropentadienyl)metal complexes: i.e., complexes in which one of the terminal CH_2 groups of the pentadienyl chain has been replaced by a heteroatom such as O, N, P, or S.[3] Like their pentadienyl analogues, these complexes are expected to exhibit a variety of bonding modes and a rich reaction chemistry based on facile ligand rearrangements.

Our previous work in this area has focused on the systematic synthesis of (heteropentadienyl)iridium complexes, using haloiridium phosphine precursors and anionic heteropentadienide reagents (including oxapentadienide,[4] thiapentadienide,[5] phosphapentadienide,[6] and azapentadienide[7]) as the building blocks. This work has also led to the production of a series of novel aromatic metallacycles, including iridafuran,[8] iridapyrylium,[9] iridathiophene,[10] and iridathiabenzene.[11] More recently, we have begun a systematic exploration of (heteropentadienyl)rhodium phosphine chemistry,[12] and in this communication we report our initial findings on the (thiapentadienyl)rhodium reaction system.

Scheme 1



1 **A**

As shown in Scheme 1, treatment of (Cl)Rh(PMe$_3$)$_3$[13] with the anionic thiapentadienide reagent lithium 2,3-dimethyl-5-thiapentadienide[11b] leads to the production of ((1,2,5-η)-2,3-dimethyl-5-thiapentadienyl)Rh(PMe$_3$)$_3$ (**1**).[14] The η^3 bonding mode of the thiapentadienyl ligand in **1** is evident from the ^{1}H and ^{13}C{^{1}H} NMR spectra. In the ^{1}H NMR, H4 resonates at a typical olefinic value of δ 5.74, while the H1's are shifted substantially upfield to δ 2.53 and 2.21. Similarly, in the ^{13}C{^{1}H} NMR the

(1) Pentadienyl−Metal−Phosphine Chemistry. 32. Part 31: Bleeke, J. R.; Donnay, E.; Rath, N. P. *Organometallics* **2002**, *21*, 4099.

(2) For reviews, see: (a) Ernst, R. D. *Chem. Rev.* **1988**, *88*, 1255. (b) Yasuda, H.; Nakamura, A. *J. Organomet. Chem.* **1985**, *285*, 15. (c) Powell, P. *Adv. Organomet. Chem.* **1986**, *26*, 125. (d) Ernst, R. D. *Comments Inorg. Chem.* **1982**, *21*, 285.

(3) For some previous examples of thiapentadienyl (or "butadienethiolate") metal complexes, see: (a) Spies, G. H.; Angelici, R. J. *Organometallics* **1987**, *6*, 1897. (b) Hachgenei, J. W.; Angelici, R. J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 909. (c) Hachgenei, J. W.; Angelici, R. J. *J. Organomet. Chem.* **1988**, *355*, 359. (d) Skaugset, A. E.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics* **1990**, *9*, 2875. (e) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P.; Herrera, V.; Sanchez-Delgado, R. A. *J. Am. Chem. Soc.* **1993**, *115*, 2731. (f) Bianchini, C.; Jimenez, M. V.; Meli, A.; Vizza, F. *Organometallics* **1995**, *14*, 3196. (g) Bianchini, C.; Jimenez, M. V.; Meli, A.; Vizza, F. *Organometallics* **1995**, *14*, 4858. (h) Bianchini, C.; Jimenez, M. V.; Meli, A.; Moneti, S.; Vizza, F. *J. Organomet. Chem.* **1995**, *504*, 27. (i) Kawano, H.; Narimatsu, H.; Yamamoto, D.; Tanaka, K.; Hiraki, K.; Onishi, M. *Organometallics* **2002**, *21*, 5526.

(4) (a) Bleeke, J. R.; Haile, T.; Chiang, M. Y. *Organometallics* **1991**, *10*, 19. (b) Bleeke, J. R.; Haile, T.; New, P. R.; Chiang, M. Y. *Organometallics* **1993**, *12*, 517.

(5) (a) Bleeke, J. R.; Orthwerth, M. F.; Chiang, M. Y. *Organometallics* **1992**, *11*, 2740. (b) Bleeke, J. R.; Ortwerth, M. F.; Rohde, A. M. *Organometallics* **1995**, *14*, 2813.

(6) (a) Bleeke, J. R.; Rohde, A. M.; Robinson, K. *Organometallics* **1994**, *13*, 401. (b) Bleeke, J. R.; Rohde, A. M.; Robinson, K. D. *Organometallics* **1995**, *14*, 1674.

(7) Bleeke, J. R.; Luaders, S. T.; Robinson, K. D. *Organometallics* **1994**, *13*, 1592.

(8) Bleeke, J. R.; New, P. R.; Blanchard, J. M. B.; Haile, T.; Beatty, A. M. *Organometallics* **1995**, *14*, 5127.

(9) (a) Bleeke, J. R.; Blanchard, J. M. B. *J. Am. Chem. Soc.* **1997**, *119*, 5443. (b) Bleeke, J. R.; Blanchard, J. M. B.; Donnay, E. *Organometallics* **2001**, *20*, 324.

(10) (a) Bleeke, J. R.; Ortwerth, M. F.; Chiang, M. Y. *Organometallics* **1993**, *12*, 985. (b) Bleeke, J. R.; Ortwerth, M. F.; Rohde, A. M. *Organometallics* **1995**, *14*, 2813.

(11) (a) Bleeke, J. R.; Hinkle, P. V.; Rath, N. P. *J. Am. Chem. Soc.* **1999**, *121*, 595. (b) Bleeke, J. R.; Hinkle, P. V.; Rath, N. P. *Organometallics* **2001**, *20*, 1939.

(12) For the (oxapentadienyl)rhodium system, see ref 1.

(13) (Cl)Rh(PR$_3$)$_3$ starting materials were obtained by adding 6 equiv of PR$_3$ to [(C$_8$H$_{14}$)$_2$Rh(μ-Cl)]$_2$: van der Ent, A.; Onderdelinden, A. L. *Inorg. Synth.* **1973**, *14*, 92.

(14) Closely related rhodium complexes containing the tris-chelating phosphine ligand "triphos" have been obtained by Bianchini et al., via thiophene C−S bond cleavage.[3f,g]

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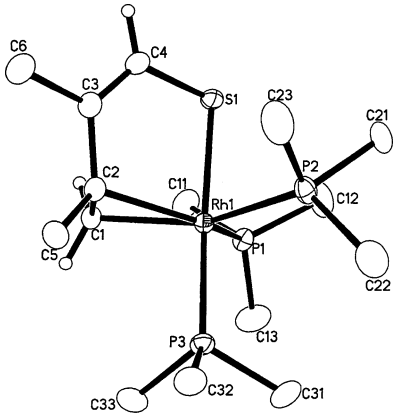


Figure 1. ORTEP drawing of **1**, using thermal ellipsoids at the 30% level. Methyl H's are not shown. Selected bond distances (Å): Rh1−P1, 2.3512(7); Rh1−P2, 2.3385(7); Rh1−P3, 2.2668(7); Rh1−S1, 2.3992(7); Rh1−C1, 2.137(2); Rh1−C2, 2.222(2); C1−C2, 1.437(4); C2−C3, 1.505(4); C3−C4, 1.339(4); C4−S1, 1.741(3).

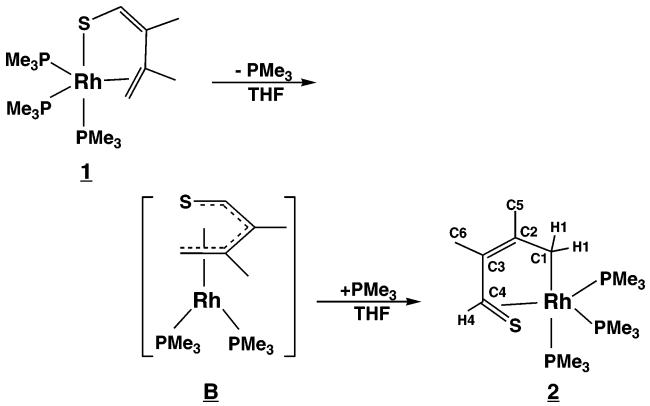
metal-coordinated carbons, C1 and C2, resonate at δ 43.9 and 73.3, respectively, while the uncoordinated carbons, C3 and C4, appear downfield at δ 139.4 and 121.8, respectively.

At room temperature, the $^{31}P\{^1H\}$ NMR spectrum exhibits a deceptively simple pattern consisting of doublet of triplets (intensity 1) and doublet of doublets (intensity 2). The large doublet splitting in each case is due to rhodium−phosphorus coupling, while the smaller triplet or doublet splitting is a phosphorus−phosphorus coupling. The simplicity of the pattern results from a rapid solution-phase dynamic process in which the double bond C1−C2 undergoes dissociation from the rhodium center and reassociation (see Scheme 1). The 16e$^-$ dissociated intermediate (**A**; Scheme 1)[15] possesses mirror-plane symmetry, leading to the observed equivalence of the mutually trans phosphines by NMR. Upon cooling to −70 °C, the dynamic process is slowed, and separate signals for the three inequivalent phosphines are observed. When excess PMe_3 is added to **1** at room temperature, a broad hump is observed in the $^{31}P\{^1H\}$ NMR, indicating that the added (free) phosphine is exchanging with the coordinated PMe_3 ligands. This phosphine exchange process probably proceeds by addition of PMe_3 to 16e$^-$ intermediate **A** (Scheme 1), followed by phosphine loss.

The structure of compound **1** has been confirmed by single-crystal X-ray diffraction and is presented in Figure 1. The coordination geometry about rhodium is a distorted octahedron with S1 and P3 occupying the axial sites and C1, C2, P1, and P2 defining the equatorial plane. As expected, the C1−C2 distance has lengthened to 1.437(4) Å as a result of its coordination to the rhodium center, while the C2−C3 and C3−C4 bond lengths are typical for C−C single and double bonds, respectively. The phosphorus atom P3, which is situated trans to S1, displays a significantly shorter bond to rhodium than do P1 and P2, which reside opposite carbon atoms.

When compound **1** is stirred in tetrahydrofuran for 48 h, it gradually isomerizes to ((1,4,5-η)-2,3-dimethyl-5-thiapentadienyl)Rh(PMe_3)$_3$ (**2**; Scheme 2), in which the thiapentadienyl ligand is σ-bonded to rhodium through the carbon end of the chain (C1) and π-bound through

Scheme 2



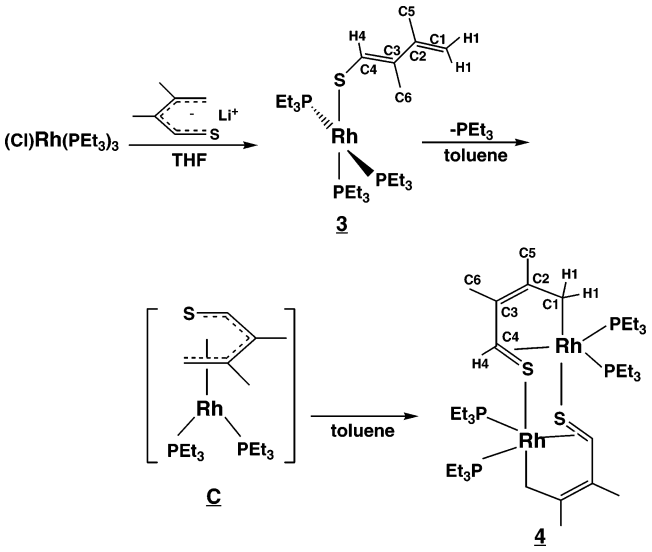
the sulfur end (double bond C4−S). As before, the ^1H and $^{13}C\{^1H\}$ NMR spectra of **2** are diagnostic. In the ^1H NMR, the signal for H4 is shifted upfield to δ 4.09 (from its position at δ 5.74 in **1**), while the H1's are likewise shifted upfield to δ 2.25 and 1.10 (from δ 2.53 and 2.21 in **1**). In the $^{13}C\{^1H\}$ spectra, the π-coordinated carbon C4 resonates at δ 73.6 (vs δ 121.8 in **1**), while the σ-coordinated carbon C1 appears at δ 32.2 and is strongly coupled to a trans PMe_3 ligand (J_{C-P} = 98.8 Hz). Uncoordinated carbons C2 and C3 resonate at δ 142.0 and 136.0. Unlike **1**, compound **2** is not fluxional at room temperature and gives rise to three well-separated doublet of doublets of doublets patterns in the $^{31}P\{^1H\}$ NMR. For each signal, the largest splitting is due to rhodium−phosphorus coupling, while the smaller splittings are phosphorus−phosphorus couplings. In the presence of excess PMe_3, the conversion of **1** to **2** is completely shut down, strongly implying that a PMe_3 dissociation is required. This, in turn, suggests that an η^5-thiapentadienyl species (**B**; Scheme 2) may serve as a key intermediate.

When (Cl)Rh(PEt_3)$_3$ is treated with lithium 2,3-dimethyl-5-thiapentadienide, the product is an η^1-thiapentadienyl species, ((5-η)-2,3-dimethyl-5-thiapentadienyl)Rh(PEt_3)$_3$ (**3**; Scheme 3). The increased steric bulk of the PEt_3 ligands is apparently responsible for the 16e η^1 ground-state structure. Furthermore, structural evidence presented below strongly implies that the η^1-thiapentadienyl ligand in **3** possesses a trans internal double bond (C3−C4), in contrast to the cis internal double bond in **1** and in the lithium thiapentadienide starting material. This rearrangement, which probably proceeds through a transient C3-bound (η^1-thiapentadienyl)rhodium intermediate, minimizes steric contacts between the thiapentadienyl chain and the PEt_3 ligands.

In the ^1H and $^{13}C\{^1H\}$ NMR spectra of **3**, all of the thiapentadienyl signals appear in the downfield (uncoordinated) region. H4 resonates at δ 7.05, while the two H1's resonate at δ 4.7 and 4.6; the thiapentadienyl carbons appear at δ 144.9 (C2), 138.7 (C4), 130.2 (C3), and 104.9 (C1). The $^{31}P\{^1H\}$ NMR spectrum consists of just two signals, a doublet of doublets (intensity 2) and a doublet of triplets (intensity 1), consistent with a square-planar complex possessing mirror plane symmetry. The spectrum does not change upon cooling.

(15) The 16e intermediate **A** can be "trapped" by exposing compound **1** to air. The resulting peroxo product, ((5-η)-2,3-dimethyl-5-thiapentadienyl)Ir(η^2-O_2)(PMe_3)$_3$, has been characterized by a preliminary X-ray study: Bleeke, J. R.; Wise, E. S.; Rath, N. To be submitted for publication.

Scheme 3



When compound **3** is stirred in toluene at room temperature, the sulfur-bridged dimer **4** (see Scheme 3) is gradually formed. In this dimer, as in compound **2**, the thiapentadienyl ligand has rearranged so that the carbon end of the chain (C1) is σ-bonded to rhodium, while the sulfur end (double bond C4−S) is π-bound. As before, an (η^5-thiapentadienyl)Rh(PR_3)$_2$ species (**C**; Scheme 3) appears to be a likely intermediate. The steric bulk of triethylphosphine promotes *dimerization* to **4** rather than ligand readdition to form the monomeric tris-PEt_3 analogue of **2**.

The ^{1}H and ^{13}C NMR spectra of **4** are very similar to those of compound **2**. The signal for H4 appears at δ 4.55, while the two H1's resonate at δ 1.12 and 0.85. The π-bound carbon C4 appears at δ 76.4, while the σ-bound carbon C1 resonates at δ 23.7 and uncoordinated carbons C2 and C3 resonate at δ 138.9 and 137.8. The ^{31}P{^{1}H} NMR spectrum of **4** consists of two doublet of doublets patterns, where the larger splitting is due to rhodium−phosphorus coupling while the smaller separation is due to phosphorus−phosphorus coupling.

The structure of **4** has been confirmed by X-ray diffraction and is presented in Figure 2. The dimeric molecule sits on a crystallographically imposed inversion center, and the coordination geometry around each rhodium is best described as distorted octahedral. Ring carbon C1 and the bridging sulfur of the other monomer (S1′) occupy trans-diaxial sites, while C4, S1, P1, and P2 occupy equatorial sites. The carbon−carbon bonds within the thiapentadienyl ligand exhibit the expected single−double−single alternation, and the carbon−sulfur bond distance of 1.789(3) Å is close to that of a typical single bond (1.82 Å).[16] This C−S bond distance, together with the short Rh−C4 distance of 2.071(3) Å, suggests strong π-back-bonding into the C−S π^* orbital. Phosphorus atom P1, which is situated trans to sulfur S1, displays a significantly shorter bond to rhodium than does P2, which lies trans to C4. This difference in bond distances is also reflected in the ^{31}P NMR coupling constants, wherein J_{Rh-P1} = 166.7 Hz while J_{Rh-P2} = 119.8 Hz.

When compound **3** is stirred in acetone, a second dimeric product, containing bridging S-bound η^1-thiapentadienyl ligands, can be isolated (**5**; Scheme 4).

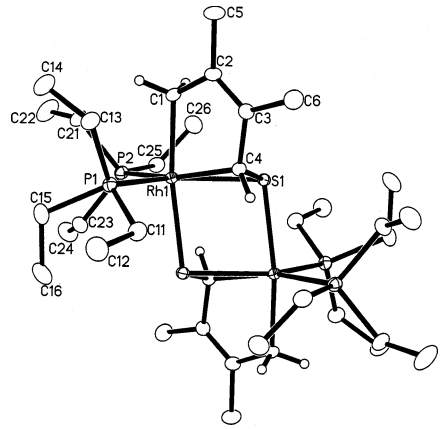
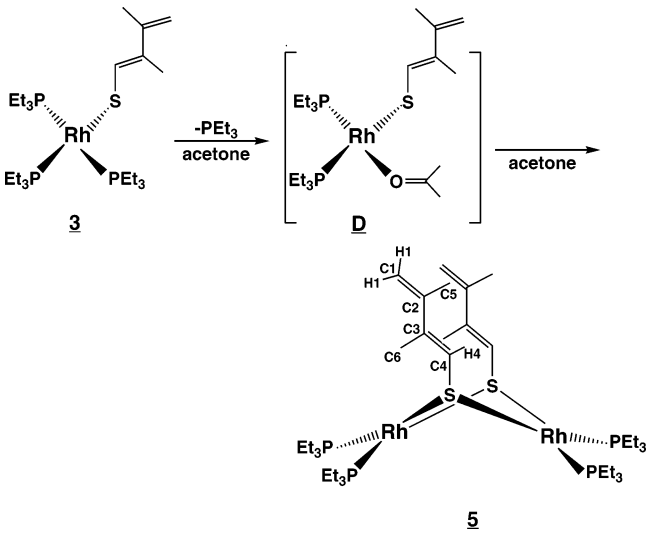


Figure 2. ORTEP drawing of **4**, using thermal ellipsoids at the 30% level. Methyl and ethyl H's are not shown. Selected bond distances (Å): Rh1−P1, 2.2641(7); Rh1−P2, 2.3644(7); Rh1−S1, 2.4126(6); Rh1−S1′, 2.4604(6); Rh1−C1, 2.100(3); Rh1−C4, 2.071(3); C1−C2, 1.495(4); C2−C3, 1.332(4); C3−C4, 1.495(4); C4−S1, 1.789(3).

Scheme 4



Apparently, this product is generated because the acetone solvent traps the phosphine-dissociated intermediate (**D**; Scheme 4) before the thiapentadienyl double bonds can coordinate to rhodium. In the absence of a coordinating solvent (e.g., toluene), the thiapentadienyl double bonds coordinate, leading to thiapentadienyl ligand isomerization and formation of dimer **4** (cf., Scheme 3). The ^{1}H and ^{13}C{^{1}H} NMR spectra of **5** are diagnostic for the S-bound η^1-thiapentadienyl bonding mode and bear a close resemblance to those of **3**. In particular, the thiapentadienyl protons resonate downfield at δ 6.96 (H4), 4.74 (H1) and 4.66 (H1), while the thiapentadienyl carbons resonate at δ 146.2 (C2), 134.7 (C3), 133.7 (C4), and 107.8 (C1). Because all four PEt_3 ligands are chemically equivalent, the ^{31}P{^{1}H} NMR signal is a simple rhodium-coupled doublet.

The structure of **5** has been confirmed by X-ray diffraction and is presented in Figure 3. The Rh_2S_2 core of **5** is bent with Rh−S−Rh hinge angles of 87.10(3) and 87.93(3)° and a Rh−Rh separation of 3.304 Å.[17] The

(16) Huheey, J. E. *Inorganic Chemistry: Principles of Structure and Reactivity*; Harper & Row: New York, 1972; Appendix F, and references therein.

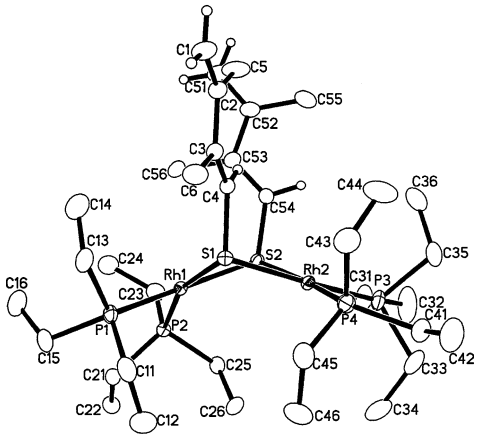


Figure 3. ORTEP drawing of **5**, using thermal ellipsoids at the 30% level. Methyl and ethyl H's are not shown. Selected bond distances (Å): Rh1−P1, 2.2470(9); Rh1−P2, 2.2533(9); Rh1−S1, 2.3850(8); Rh1−S2, 2.3722(8); C1−C2, 1.335(5); C2−C3, 1.465(4); C3−C4, 1.346(4); C4−S1, 1.765(3); Rh2−P3, 2.2378(9); Rh2−P4, 2.2466(9); Rh2−S1, 2.4111(8); Rh2−S2, 2.3876(8); C51−C52, 1.337(5); C52−C53, 1.476(5); C53−C54, 1.348(4); C54−S2, 1.753(3).

η^1-thiapentadienyl ligands adopt a "syn exo" orientation, in which they are both directed *away from* the PEt_3 ligands for steric reasons (the torsional angle C4−S1−S2−C54 is 3.8°). The thiapentadienyl ligand planes are essentially perpendicular to one another (the dihedral angle between the planes C1/C2/C3/C4/S1 and C51/C52/C53/C54/S2 is 102.9°), and the ligands themselves are both W-shaped with trans geometries around the internal double bonds C3−C4 and C53−C54. When **5** is treated with excess PEt_3 at room temperature in tetrahydrofuran, it readily converts back to **3**, which strongly implies that the η^1-thiapentadienyl ligand in **3** also possesses a trans internal double bond (vide supra).

In conclusion, we have explored the reactivity of $(Cl)Rh(PR_3)_3$ (R = Me, Et) with an anionic thiapentadienide reagent, lithium 2,3-dimethyl-5-thiapentadienide. In each case, the kinetic product exhibits a thiapentadienyl bonding mode in which the sulfur atom is σ-bonded to the rhodium center—1,2,5-η^3 in the PMe_3 system and 5-η^1 in the PEt_3 system. However, these initial products both isomerize to thermodynamic products displaying the 1,4,5-η^3 bonding mode, wherein the carbon end of the thiapentadienyl ligand is σ-bonded to the rhodium center. In the PMe_3 system, the product remains monomeric, but the bulkier PEt_3 product loses a phosphine and dimerizes through sulfur atom bridges. The accessibility of multiple thiapentadienyl bonding modes in these complexes implies a rich and varied reaction chemistry; these studies are currently under active investigation in our laboratory.

Acknowledgment. Support from the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We also thank Pfizer Global Research and Development for a Summer Undergraduate Research Fellowship to E.S.W. Washington University's High Resolution NMR Service Facility was funded in part by NIH Support Instrument Grants (RR-02004, RR-05018, and RR-07155).

Supporting Information Available: Text giving detailed synthetic procedures for compounds **1**−**5**, including spectroscopic data, and structure determination summaries and listings of final atomic coordinates, thermal parameters, bond lengths, and bond angles for compounds **1**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) The bending is due to the sulfur's preference to be highly pyramidalized and to the presence of a weak Rh−Rh bonding interaction: Oster, S. S.; Jones, W. D. *Inorg. Chim. Acta* **2004**, *357*, 1836.