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# Structural properties and inversion mechanisms of [Rh(dippe)(µ-SR)]<sub>2</sub> complexes

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#### Abstract

Several new bis-thiolate complexes of the type  $[Rh(dippe)(\mu-SR)]_2$  where R = H, methyl, cyclohexyl, *o*-biphenyl, and phenyl, or  $(SR)_2=SCH_2CH_2CH_2CH_2S$  have been synthesized and characterized by NMR spectroscopy and single crystal X-ray diffraction. All  $[Rh(dippe)(\mu-SR)]_2$  complexes except  $[Rh(dippe)(\mu-SPh)]_2$  exhibit bent geometries, while the orientation of the thiolato substituents changes with increasing steric bulk. <sup>1</sup>H and <sup>31</sup>P NMR spectroscopies indicate that both ring inversion and sulfur inversion occur among the members of the series, which allows them to access several isomeric forms when they are in solution. <sup>31</sup>P NMR spectroscopy indicates that sulfur inversion in  $[Rh(dippe)(\mu-SH)]_2$ ,  $[Rh(dippe)(\mu-Sbiphenyl)]_2$ , and  $[Rh(dippe)(\mu-SPh)]_2$  is a non-dissociative process. © 2003 Elsevier B.V. All rights reserved.

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# 1. Introduction

The existence of binuclear metal complexes that possess a  $M_2S_2$  core is well established in the literature. One salient feature is that they can exist in a number of distinct conformations. For example,  $[M_2(\mu-S)_2L_4]$ complexes can exist as either planar or bent conformers. The addition of R groups to the  $M_2S_2$  core further expands the number of possible isomers.  $[M_2(\mu-S)(\mu-SR)L_4]$  complexes, where R = H, alkyl, or aryl, may be found in a total of four, and  $[M_2(\mu-SR)_2L_4]$  complexes may be found in a total of six, distinct conformations. Sulfur strongly prefers a pyramidal geometry, so the bent complexes predominate in the structures that have been characterized [1].

A second feature that is related to the first is that complexes of the three bent-dialkyl type shown in Scheme 1 are often fluxional on the NMR timescale [2–8]. Consequently, all three classes of complexes interconvert between at least some of their possible conformations. One fluxional process that involves the entire  $M_2S_2$  core is *ring inversion*, which is analogous to chairchair interconversion in cyclohexane. Another process, which appears to have a higher energy barrier than ring inversion, is *sulfur inversion*. Here, the sulfur lone pair inverts at the M–( $\mu$ -SR)–M linkage. This can occur by either a dissociative or non-dissociative mechanism. In the dissociative case, a dative bond is broken between the sp<sup>3</sup>-hybridized sulfur and one metal atom. Rotation about the remaining sulfur–metal bond is followed by reformation of a Rh–S bond with a different pair of electrons. In the non-dissociative case, the sulfur atom proceeds through a planar transition state in which it is sp<sup>2</sup>-hybridized. It is well known that sulfur also inverts when it is attached to a metal center as part of a terminal ligand and when it is part of an organic ring [9–15].

Recently, a study that investigated the structure, reactivity, and fluxional behavior of  $[Ni(dippe)(\mu-S)]_2$  and its reaction products has been reported [16]. Like other sulfur-bridged transition metal complexes, they too interconvert between their possible conformers by a process that is most likely ring inversion, also called ringflip, of the M<sub>2</sub>S<sub>2</sub> core. However, experimental evidence suggested the presence of sulfur inversion, as well. Moreover, Torrens and coworkers [17] also recently

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Scheme 1.

reported the results of a study in which  $(Bu_4N)_2[Pt_2-(\mu-SC_6F_5)_2(SC_6F_5)_4]$ ,  $(Bu_4N)_2$   $[Pt_2(\mu-SC_6HF_4)_2(SC_6HF_4)_4]$ , and  $(Bu_4N)_2[Pt_2(\mu-p-SC_6F_4(CF_3))_2(p-SC_6F_4(CF_3))_4]$  appear to undergo inversion at the bridging sulfur atoms. Since then, in HDS studies,  $[Rh(dippe)(\mu-S-2-biphenyl)]_2$  and  $[Rh(dippe)(\mu-SPh)]_2$  were independently synthesized to determine if they occur as reaction products, and in turn they became an interesting subject in their own right. Several analogs of these two species were then synthesized and studied. Herein is a report on the synthesis, structural properties, and NMR spectral characteristics of  $[Rh(dippe)(\mu-SR)]_2$  complexes, where R = H, alkyl, and aryl groups, and a comparison is made among them, as well as to similar complexes that have been documented in the literature.

#### 2. Experimental

All operations were performed under a nitrogen atmosphere unless otherwise stated. C<sub>6</sub>D<sub>6</sub>, THF, THF-d<sub>8</sub>, hexanes, and toluene-d<sub>8</sub> were distilled from dark purple solutions of benzophenone ketyl. Thiophenol and cyclohexanethiol were purchased from Aldrich Chemical Co., and distilled from CaCl<sub>2</sub>. NaSH, and NaSCH<sub>3</sub> were purchased from Aldrich Chemical Co. and used without further purification. 2-Phenylthiophenol was obtained from John C. DiCesare, Department of Chemistry, University of Tulsa, Tulsa, Oklahoma, and used without further purification. A Siemens-SMART 3-Circle CCD diffractometer was used for X-ray crystal structure determinations. Elemental analyses were obtained from Desert Analytics and Complete Analysis Laboratories, Incorporated. All <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra were recorded on a Bruker Avance 400 NMR spectrometer. All <sup>1</sup>H chemical shifts are reported relative to the residual proton resonance in the deuterated solvent. All <sup>31</sup>P chemical shifts are reported relative

to the signal of 85% H<sub>3</sub>PO<sub>4</sub>. [Rh(dippe)( $\mu$ -Cl)]<sub>2</sub> and [Rh(dippe)( $\mu$ -H)]<sub>2</sub> have been previously synthesized and fully characterized [18,19]. Details of the X-ray structure determinations are given in the Supplementary Material.

# 2.1. Synthesis of $[Rh(dippe)(\mu-SH)]_2$ (1)

Ten equivalents of NaSH (192 mg, 3.4 mmol) was added, all at once, to a stirred THF suspension of [Rh(dippe)Cl]<sub>2</sub> (274 mg, 0.34 mmol) in approximately 50 mL of THF. The mixture was stirred overnight and then filtered through 80-200 mesh neutral alumina on a fine glass frit to remove unreacted NaSH and NaCl. The solvent was evaporated to dryness under vacuum. The solid was extracted with 5 mL portions of hexanes, which were combined and placed under vacuum to evaporate the solvent and leave a yellow solid (169 mg, 61.3%). Crystals for X-ray structural analysis were grown from a THF solution of the product at -30 °C. <sup>1</sup>H NMR (400 MHz, THF-d<sub>8</sub>, 20 °C): δ 2.07 (sext, J = 6.9 Hz, 8H), 1.38 (d, J = 12.0 Hz, 8H), 1.30–1.25 (dd, J = 7.1, 7.0 Hz, 24H), 1.20-1.06 (dd, J = 6.8, 5.0)Hz, 24H), -1.37 (s, 2H). <sup>13</sup>C NMR (100 MHz, THF-d<sub>8</sub>, 25 °C): 27.90 (m), 23.19 (m), 20.76 (s), 19.13 (s). <sup>31</sup>P NMR (162 MHz, THF-d<sub>8</sub>, 20 °C): δ 93.16 (d,  $J_{(P-Rh)} = 176.6$  Hz). Anal. Calc. (Found) for  $\dot{C}_{28}H_{66}^{'}Rh_2P_4S_2$ : C, 42.21 (42.36); H, 8.35 (8.66)%.

# 2.2. Synthesis of $[Rh(dippe)(\mu-SCH_3)]_2$ (2)

Approximately 4.3 equivalents of NaSCH<sub>3</sub> (118 mg, 1.69 mmol) was added, all at once, to a stirred THF suspension of [Rh(dippe)Cl]<sub>2</sub> (312 mg, 3.89 mmol) in approximately 50 mL of THF. The mixture was stirred overnight and then filtered through 80-200 mesh neutral alumina on a fine glass frit to remove unreacted NaSCH<sub>3</sub> and NaCl. The solvent was evaporated to dryness under vacuum to leave a yellow solid (119 mg, 37.1%). Crystals for X-ray structural analysis were grown from a THF solution of the product at -30 °C. <sup>1</sup>H NMR (400 MHz, THF-d<sub>8</sub>, 30 °C): δ 2.23 (s, 6H), 2.14–2.05 (m, 8H), 1.35 (d,  $J_{(H-P)} = 11.5$  Hz, 8H), 1.34– 1.28 (dd, J = 7.4, 7.1 Hz, 24H), 1.13–1.09 (dd, J = 7.0, 4.4 Hz, 24H). <sup>13</sup>C NMR (100 MHz, THF-d<sub>8</sub>, 25 °C):  $\delta$ 27.55 (t, J = 9.6 Hz), 22.87 (td, J = 20.9, 3.6 Hz), 21.07 (s), 19.58 (s), 19.24 (s). <sup>31</sup>P NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>, 20 °C):  $\delta$  90.83 (d,  $J_{(P-Rh)} = 172.2$  Hz). *Anal*. Calc. (Found) for C<sub>30</sub>H<sub>70</sub>Rh<sub>2</sub>P<sub>4</sub>S<sub>2</sub>: C, 43.69 (43.97); H, 8.56 (8.62)%.

# 2.3. Synthesis of $[Rh(dippe)(\mu-SC_6H_{11})]_2$ (3)

Approximately 2.05 equivalents of cyclohexanethiol (0.069 mL, 0.57 mmol) was added via syringe to a stirred hexanes solution ( $\cong$ 25 mL) of [Rh(dippe)H]<sub>2</sub> (202 mg, 0.28 mmol). A reaction immediately occurred as H<sub>2</sub> evolved and the color of the solution turned from

emerald green to orange. The mixture was stirred for 15 min and then the solvent was evaporated to dryness under vacuum to yield an orange solid. The solid was washed twice with pentane to remove residual cyclohexanethiol and then dried under vacuum (114 mg, 43.6%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>H<sub>6</sub>, 20 °C):  $\delta$  3.27 (bt, J = 11.2 Hz, 2H), 2.84 (bd, J = 12.3 Hz, 4H), 2.31–2.22 (m, 6.9 Hz, 8H), 1.95 (bd, J = 12.8 Hz, 4H), 1.36–1.71 (m, 8H), 1.58 (dd, J = 7.0, 6.4 Hz, 24H), 1.36–1.22 (m, 4H), 1.15 (m, J = 6.9, 4.5 Hz, 24H), 1.06 (d, J = 12.5 Hz, 8H). <sup>13</sup>C NMR (100 MHz, THF-d<sub>8</sub>, 25 °C):  $\delta$  47.20 (s), 42.70 (s), 29.36 (s), 27.99 (m), 27.15 (s), 23.35 (m), 21.41 (s), 19.17 (s). <sup>31</sup>P NMR (162 MHz, THF-d<sub>8</sub>, 20 °C):  $\delta$  82.73 (d,  $J_{(P-Rh)} = 171.8$  Hz). *Anal.* Calc. (Found) for C<sub>40</sub>H<sub>86</sub>Rh<sub>2</sub>P<sub>4</sub>S<sub>2</sub>: C, 49.99 (49.86); H, 9.02 (9.04)%.

# 2.4. Synthesis of $[Rh(dippe)(\mu-SC_{12}H_9)]_2$ (4)

Approximately 2.05 equiv. of 2-phenylthiophenol (50.9 mg, 0.27 mmol) in hexanes was added dropwise to a stirred hexanes solution (50 mL) of [Rh(dippe)H]<sub>2</sub> (97.7 mg, 0.133 mmol) as the color of the mixture immediately changed from emerald green to orange. The resulting solution was stirred for approximately 15 min and then the solvent was evaporated under vacuum to leave a rust colored solid (104 mg, 70.8%). The solid was dissolved in a minimal amount of THF and chilled at -30 °C to yield crystals that were suitable for X-ray crystal diffractometry. <sup>1</sup>H NMR (400 MHz, toluene-d<sub>8</sub>, 20 °C):  $\delta$  9.91 (d, J = 7.7 Hz), 8.93 (bs), 8.08 (bs), 8.01 (d, J = 7.1 Hz), 7.36 (bs), 7.27 (bm), 7.17 (bm), 6.78 (m),6.45 (m), 2.23 (bs), 1.86 (bs), 1.67 (bs), 1.49 (m), 1.30-0.94 (m), 0.82 (m). <sup>13</sup>C NMR (100 MHz, toluene-d<sub>8</sub>, 25 °C):  $\delta$  131.12 (s), 130.38 (s), 127.49 (s), 126.01 (s), 27.46 (m), 26.85 (s), 21.45 (s), 19.07 (s), 18.92 (s). <sup>31</sup>P NMR (162 MHz, toluene-d<sub>8</sub>, 20 °C):  $\delta$  91.22 (d,  $J_{(P-Rh)} = 178.5$ Hz), 89.02 (d,  $J_{(P-Rh)} = 178.5$  Hz) (two doublets appear in a 1:2 ratio). Anal. Calc. (Found) for C<sub>52</sub>H<sub>82</sub>Rh<sub>2</sub>P<sub>4</sub>S<sub>2</sub>: C, 56.72 (56.67); H, 7.51 (7.76)%.

#### 2.5. Alternative synthesis of 4

Approximately 2.1 equiv. of lithium 2-phenylthiophenolate (180.0 mg, 0.93 mmol) was added all at once to a hexanes suspension of  $[Rh(dippe)Cl]_2$  (354 mg, 0.44 mmol). The resulting mixture was stirred overnight. The contents of the reaction flask were vacuum filtered through 80–200 mesh neutral alumina to remove LiCl. The solvent was then evaporated under vacuum to leave 4 (366 mg, 75.3%).

#### 2.6. Synthesis of $[Rh_2(dippe)_2(\mu - S_2C_3H_6)]$ (5)

Approximately 1 equiv. of 1,3-propanedithiol (0.57 mL, 1.977 M in hexanes) was added dropwise to a stirred pentane solution (950 mL) of [Rh(dippe)H]<sub>2</sub>

(825.5 mg, 1.13 mmol). H<sub>2</sub> evolved as the solution color changed to yellow, followed by the formation of a yellow precipitate. The solvent was removed via vacuum filtration. The solid was washed twice with pentane and dried overnight under vacuum (140.6 mg, 58.0%). Approximately 20 mg of 5 was dissolved in THF and chilled to -30 °C to grow crystals that were suitable for X-ray diffraction. <sup>1</sup>H NMR (400 MHz, THF-d<sub>8</sub>, 25 °C):  $\delta$  2.77 (s, 4H), 2.27–2.07 (m, 10H), 1.39–1.34 (dd, J = 6.9, 6.5 Hz, 12H), 1.32 (bs, 8H), 1.26–1.21 (dd, J = 7.2, 7.1 Hz, 12H), 1.16–1.11 (dd, J = 6.9, 5.5 Hz, 12H), 1.09–1.05 (dd, J = 7.0, 4.2 Hz, 12H). <sup>13</sup>C NMR (100 MHz, THF-d<sub>8</sub>, 25 °C): δ 40.99 (s), 34.68 (s), 28.27 (t, J = 10.5 Hz), 26.96 (t, J = 16.6 Hz), 23.25 (td, J = 20.6, 3.8 Hz), 21.56 (s), 20.20 (s), 19.77 (s), 18.82 (s). <sup>31</sup>P NMR (162 MHz, THF-d<sub>8</sub>, 25 °C): δ 88.09 (d, J = 171.7 Hz). Anal. Calc. (Found) for  $C_{31}H_{70}Rh_2P_4S_2$ : C, 44.14 (44.41); H, 8.37 (8.60)%.

# 2.7. Synthesis of $[Rh(dippe)(\mu-SC_6H_5)]_2$ (6)

Approximately 2.05 equivalents of benzenethiol (0.58 mL, 0.56 mmol) was added via syringe to a stirred hexanes solution (25 mL) of [Rh(dippe)H]<sub>2</sub> (201 mg, 0.27 mmol). A reaction immediately occurred as H<sub>2</sub> evolved and the color of the solution turned from emerald green to yellow. The mixture was stirred for 15 min and then the solvent was evaporated to dryness under vacuum to yield a yellow solid. The solid was washed three times with hexanes to remove residual benzenethiol and then dried under vacuum (222 mg, 85.4%). <sup>1</sup>H NMR (400 MHz, THF-d<sub>8</sub>, 20 °C): δ 7.94 (m, 4H), 6.81 (m, 6H), 1.81 (sept, J = 6.9 Hz, 8H), 1.25 (d, J = 12.0 Hz, 8H), 1.19–1.01 (m, 48H). <sup>13</sup>C NMR (100 MHz, THF-d<sub>8</sub>, 25 °C): δ 137.05 (s), 131.98 (s), 126.67 (s), 123.68 (s), 119.97 (s), 65.75 (s), 26.97 (m), 22.54 (m), 20.69 (s), 19.06 (s). <sup>31</sup>P NMR (162 MHz, THF-d<sub>8</sub>, 20 °C):  $\delta$  89.45 (d,  $J_{(P-Rh)} = 173.6$  Hz). Anal. Calc. (Found) for C<sub>40</sub>H<sub>74</sub>Rh<sub>2</sub>P<sub>4</sub>S<sub>2</sub>: C, 50.63 (49.83); H, 7.86 (7.78)%.

#### 2.8. Synthesis of lithium 2-phenylthiophenolate

Approximately 1 equiv. of *n*-butyllithium in hexanes (1.76 mL, 1.6 M) was added dropwise, over a two minute period, to a stirred diethyl ether solution (50 mL) of 2-phenylthiophenol (524.6 mg, 2.82 mmol). The resulting solution was stirred for 4 h to produce a white precipitate. The solvent was removed by vacuum filtration and the solid was dried under vacuum (510.1 mg, 93.3%).

#### 2.9. X-ray structures of 1-6

A Siemens-SMART CCD area detector diffractometer equipped with an LT-2 low temperature unit was used for X-ray crystal structure determination. Single crystals

Table 1 Summary of crystallographic data for 1–6

Crystal parameters	1	2	3	4	5	6
Chemical formula	$C_{28}H_{66}P_4Rh_2S_2\\$	$C_{30}H_{70}P_4Rh_2S_2\\$	$C_{40}H_{86}P_4Rh_2S_2\\$	$\begin{array}{c} C_{60}H_{98}P_4Rh_2S_2\\ \cdot 2C_4H_8O_2 \end{array}$	$C_{31}H_{70}P_4Rh_2S_2\\$	$C_{40}H_{74}P_4Rh_2S_2\\$
Formula weight	796.63	824.68	960.91	1245.20	836.69	948.81
Crystal system	monoclinic	orthorhombic	monoclinic	triclinic	triclinic	orthorhombic
Space group, Z	$P2_1/n, 4$	$P2_12_12_1, 4$	$P2_1/n, 4$	$P\overline{1}, 2$	$P\overline{1}, 2$	Cmca, 4
a (Å)	10.7900(6)	14.8813(10)	10.4590(6)	12.0877(11)	9.9435(6)	24.204(2)
b (Å)	25.5880(13)	5.4204(10)	21.7196(13)	12.4401(11)	13.1478(8)	9.1172(8)
<i>c</i> (Å)	13.4002(7)	16.8552(11)	20.7150(12)	21.538(2)	15.8197(10)	20.0689(19)
α (°)	90	90	90	96.901(2)	82.8660(10)	90
β (°)	102.6560(10)	90	97.4030(10)	104.197(2)	86.3790(10)	90
γ (°)	90	90	90	95.162(2)	71.3120(10)	90
Volume (Å <sup>3</sup> )	3609.8(3)	3867.9(4)	4666.5(5)	3093.0(5)	1943.4(2)	4428.6(7)
Temperature (°C)	-80	-80	-80	-80	-80	-80
$\rho_{\rm calc} \ ({\rm g} \ {\rm cm}^{-3})$	1.466	1.416	1.368	1.337	1.430	1.423
Number of of data collected	23555	14306	29017	13957	12668	12389
Number of unique data	8673	8139	11070	8821	8938	2708
Number of parameters varied	333	361	449	597	352	124
$R_1(F_0), wR_2(F_0^2), (I > 2\sigma(I))$	0.0387, 0.0755	0.0209, 0.0437	0.0483, 0.0933	0.1260, 0.2148	0.0242, 0.0663	0.0376, 0.1359
$R_1(F_o)$ , $wR_2(F_o^2)$ , all data	0.0570, 0.0806	0.0230, 0.0443	0.0713, 0.1006	0.1393, 0.2191	0.0281, 0.0683	0.0550, 0.1420
Goodness-of-fit	1.009	0.998	1.069	1.513	1.024	1.100

of 1-6 were mounted under Paratone-8277 on glass fibers and immediately placed in a cold nitrogen stream at -80°C on the X-ray diffractometer. The X-ray intensity data were collected on a standard Siemens-SMART CCD Area Detector System equipped with a normal focus molybdenum-target X-ray tube operated at 2.0 kW. A total of 1321 frames of data (1.3 hemispheres) were collected using a narrow frame method with scan widths of  $0.3^{\circ}$  in  $\omega$  and exposure times of 5 s/frame using a detector-to-crystal distance of 5.09 cm (maximum  $2\theta$  angle of  $56.54^{\circ}$ ) for all of the crystals except **3** (30 s), **5** (30 s), and 6 (60 s). Frames were integrated with the Siemens SAINT program to 0.75 Å for all of the data sets; however, weak data  $>46.6^{\circ}$  were omitted from the refinement of 5. The unit cell parameters for all of the crystals were based upon the least-squares refinement of three dimensional centroids of >5000 reflections.<sup>1</sup> Data were corrected for absorption using the program SADABS [20]. Space group assignments were made on the basis of systematic absences and intensity statistics by using the XPREP program (Siemens, SHELXTL 5.04). The structures were solved by using direct methods and refined by full-matrix least-squares on  $F^2$ .<sup>2</sup> For all of the structures, the non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogens were included in idealized positions giving data:parameter ratios greater than 10:1. The sulfur-bound hydrogens in 1 were

located from the difference Fourier map and the positional and isotropic thermal parameters were refined. There was nothing unusual about the solution or refinement of any of the structures, with the exception of **4**, which also contained two diffuse THF molecules within the asymmetric unit that were refined isotropically. Further experimental details of the X-ray diffraction studies are provided in Table 1.

#### 3. Results and discussion

3.1. Structural characteristics of  $[Rh(dippe)(\mu-SR)]_2$  complexes

The bridging thiolate complexes of the type  $[Rh(dippe)(\mu-SR)]_2$  are easily prepared either by reaction of  $[Rh(dippe)(\mu-Cl)]_2$  with thiolate salt or by reaction of thiol with  $[Rh(dippe)(\mu-H)]_2$  (Scheme 2).  $[Rh(dippe)(\mu-SH)]_2$  (1) is the simplest derivative in this class of complexes. Its <sup>1</sup>H NMR spectrum at 20 °C indicates the presence of two sulfhydryl groups, which appear as singlet at  $\delta$  –1.37. Also, its <sup>31</sup>P NMR spectrum at the same temperature shows a doublet that corresponds to the four equivalent phosphorus nuclei that are each coupled to I = 1/2 rhodium. The ORTEP diagram of 1, shown in Fig. 1, illustrates the fact that it assumes a bent *syn-endo* conformation in the solid state, with a hinge angle  $\theta$  of 136.0° and a substituent angle of displacement from the S–S axis  $\tau$  of 36.05° (see Table 2). <sup>3</sup>

<sup>&</sup>lt;sup>1</sup> It has been noted that the integration program SAINT produces cell constant errors that are unreasonably small, since systematic error is not included. More reasonable errors might be estimated at  $10 \times$  the listed value.

<sup>&</sup>lt;sup>2</sup> Using the SHELX 95 package,  $R_1 = (\sum ||F_o| - |F_c||) / \sum |F_o|$ ,  $\{wR_2 = [\sum (w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}]$ , where  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$  and  $P = [f(Maximum of 0 or F_o^2) + (1 - f)F_c^2]$ .

<sup>&</sup>lt;sup>3</sup> The angles are defined as follows:



Fig. 1. ORTEP drawing of  $[Rh(dippe)(\mu-SH)]_2$  (1). Ellipsoids are shown at the 30% probability level. All hydrogen atoms are omitted for clarity, except those that are on the bridging sulfur atoms, except those that are on the bridging sulfur atoms, which are shown in refined locations.

Substitution of the sulfhydryl protons by methyl groups gives  $[Rh(dippe)(\mu-SCH_3)]_2$  (2), whose X-ray structure is shown in Fig. 2. This complex assumes a bent-*anti* conformation in the solid state. This appears to be the most stable conformation in solution, as well, as the <sup>31</sup>P NMR spectrum of 2 at -95 °C in toluene-d<sub>8</sub> consists of a pair of doublet of doublets at  $\delta$  90.83, which is indicative of AA'BB'X spin system.

The observed geometries of 1 and 2 in the solid state results from the preference of sulfur to pyramidalize, the presence of metal-metal interactions, and the presence of ligand-substituent and ligand-ligand repulsions (see Table 2). To begin, both 1 and 2 exist as bent isomers, primarily because their bridging sulfur atoms strongly



Fig. 2. ORTEP drawing of  $[Rh(dippe)(\mu$ -SCH<sub>3</sub>)]<sub>2</sub> (2). Ellipsoids are shown at the 30% probability level. All hydrogen atoms are omitted for clarity.

prefer to be sp<sup>3</sup>-hybridized relative to oxygen, as coulombic repulsion between paired electrons is less in 3p orbitals than in 2p orbitals. This is reflected by the fact that the distribution of the sum of the bond angles around sulfur,  $\sum$ , in M<sub>2</sub>SR groups, where R = H, alkyl, is centered at approximately 310-320°, while the distribution for  $M_2OR$  groups is centered near 360° [1]. The other factor responsible for the bent conformations of 1 and 2 is that rhodium constitutes the metal centers of both complexes. Rhodium orbitals are diffuse relative to transition metals that are above and to the right of it in the periodic table. This allows the metal centers of 1 and 2 to achieve a weak net-bonding interaction, via their  $d_{z^2}$  and  $p_z$  orbitals, and each complex bends along its S-S axis to create a dihedral angle  $\theta$  that is less than 140°. Good  $\sigma$ -donor ligands further improve the overlap of the rhodium orbitals by enhancing  $d_{7^2}$ -s orbital mixing. This leads to resultant  $d_{z^2}$ -orbitals that are more directed along the z-axes of the two centers [21]. As a good  $\sigma$ -donor, dippe should be expected to favor bending in both 1 and 2, provided that direct ligand-ligand steric repulsion is absent.

The two different geometries of 1 and 2 in the solid state is probably due to the increase in the steric bulk of the thiolate substituents in moving from proton to methyl group. For example, Lledós, Alvarez, and coworkers calculate that to replace the SH hydrogen

Table 2 Selected angles and sums of angles about sulfur in [Rh(dippe)(µ-SR)]<sub>2</sub> complexes

Complex	Isomer	$\sum$	θ (°)	τ	$d_{ m Rh-Rh}$ (Å)
$[Rh(dippe)(\mu-SH)]_2$ (1)	syn-endo	302.52(4)°	136.0	36.05°	3.28
$[Rh(dippe)(\mu-SCH_3)]_2$ (2)	bent-anti	297.57(12)° <sub>endo</sub> /327.71(13)° <sub>exo</sub>	124.6	$83.2^{\circ}_{endo}/16.9^{\circ}_{exo}$	3.30
$[Rh(dippe)(\mu-SC_6H_{11})]_2$ (3)	syn-exo	306.87(6)°	126.4	86.05	3.25
$[Rh(dippe)(\mu-SC_{12}H_9)]_2$ (4)	syn-exo	302.35(87)°	126.3	85.75°	3.18
$[Rh_2(dippe)_2(\mu-1,2-S_2C_3H_6)]$ (5)	syn-exo	289.44(15)°	129.1	80.65°	3.24
$[Rh(dippe)(\mu-SC_6H_5)]_2$ (6)	planar- <i>anti</i>	301.02(13)°	180	77.8°	3.63

atoms in  $[M(PH_3)_2(\mu-SH)]_2$  with methyl groups, while the complex is in the bent syn-endo conformation, increases ligand-substituent repulsion by approximately 3 kcal mol<sup>-1</sup> per substituent. Yet, substituent-substituent repulsion increases by  $\sim 5 \text{ kcal mol}^{-1}$  when the model complex assumes the bent syn-exo conformation [1]. Consequently, 2 most likely adopts a bent-anti geometry because that conformation attenuates the added ligandsubstituent repulsion of the methyl substituents relative to the sulfhydryl substituents of 1, while it all together avoids a substituent-substituent repulsion. Lastly, it is worthwhile to note that 2 stands in contrast to the isoelectronic complex,  $[Pt(PH_3)_2(\mu$ -SCH<sub>3</sub>)]<sub>2</sub><sup>2+</sup>. While this dication bears methylthiolate substituents as in 2, calculations show that it prefers to be planar rather than bent when those substituents are anti to each other, which illustrates the important role that diffuse d-orbitals play in determining geometry [22].

Members of this series with R = cyclohexyl (3), biphenyl (4), and  $CH_2CH_2CH_2$  (5) all adopt the bent synexo isomer form (Figs. 3-5). The latter, with the CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> bridge, can only adopt this isomer due to geometric constraints. As is the case for 1 and 2, these complexes bend along the bridging sulfur axis due to sulfur's preference to be highly pyramidalized and to the presence of a weak net bonding rhodium-rhodium interaction. However, the cyclohexylthiolato and biphenylthiolato substituents are much more sterically demanding than methyl, which may be the reason why they are *exo*-oriented. It is possible that the energy cost in terms of dippe-substituent repulsion that would be demanded by a bent-anti conformation is greater than the cost in terms of substituent-substituent repulsion that would be demanded by a bent syn-exo conforma-



Fig. 3. ORTEP drawing of  $[Rh(dippe)(\mu-SC_6H_{11})]_2$  (3). Ellipsoids are shown at the 30% probability level. All hydrogen atoms are omitted for clarity.



Fig. 4. ORTEP drawing of  $[Rh(dippe)(\mu-SC_{12}H_9)]_2$  (4). Ellipsoids are shown at the 30% probability level. All hydrogen atoms are omitted for clarity.



Fig. 5. ORTEP drawing of  $[Rh_2(dippe)_2(\mu-S_2C_3H_6)]$  (5). Ellipsoids are shown at the 30% probability level. All hydrogen atoms are omitted for clarity.

tion. Stated differently,  $\Delta G^{\circ}$  may be more positive for both **3** and **4** if they assume bent-*anti* geometry.

In the case of **4**, it may be possible to invoke a favorable  $\pi$ -stacking effect between the  $\alpha$ -rings of the biphenylthiolato substituents as another reason why it assumes the bent *syn-exo* conformation in the solid state. For instance, Torrens and coworkers have reported several polyfluorophenyl substituted Rh<sub>2</sub>S<sub>2</sub> complexes that exist as bent *syn-exo* isomers. In two of these – [Rh( $\mu$ -SC<sub>6</sub>F<sub>5</sub>)(COD)]<sub>2</sub> and [Rh( $\mu$ -SC<sub>6</sub>HF<sub>4</sub>) (COD)]<sub>2</sub> – the distance between the two centroids is 3.45 and 3.48 Å, respectively [23,24]. Lledós and coworkers [1] point out that this is approximately the same distance as the intermolecular distance between the C<sub>6</sub>F<sub>5</sub> groups in [Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]. However, the distance between the  $\alpha$ -ring centroids in **4** is 4.06 Å. Consequently, a  $\pi$ -stacking effect is most likely absent.

An examination of the Rh–S and Rh–P bond lengths and S–Rh–S and P–Rh–P angles of **3** and **4** indicates that there is nominal elongation of the  $P_4Rh_2S_2$  moiety in the latter to offset the potential for added ligand– substituent repulsions that accompany its larger thiolato substituents. Moreover, as Table 2 illustrates, there is hardly any change in hinge angle-size between the two complexes. It appears that the oblique orientation of the biphenylate substituents to the Rh–Rh vector in **4** compensates for their steric bulk.

The complex  $[Rh_2(dippe)_2(\mu-1,2-S_2C_3H_6)]$  (5) is forced to assume a bent-*exo* conformation by its propylene linker. As Table 2 shows, the average sum of the three bond angles around the bridging sulfur atom,  $\sum$ , is ca. 289.4°. With the exception of the *endo* substituent in **2**, this makes the sulfur atoms of **5** the most highly pyramidalized in the entire  $[Rh(dippe)(\mu-SR)]_2$  series.

The complex  $[Rh(dippe)(\mu-SC_6H_5)]_2$  (6), which is shown in Fig. 6, stands in contrast to the other members of the series of [Rh(dippe)(µ-SR)]<sub>2</sub>, and also to the similar complex  $[Rh(CO)_2(\mu-SC_6H_5)]_2$  [25], in that it has a planar rhodium-sulfur core. Its two phenyl substituents are oriented in an *anti* fashion, with an average  $\tau$  of 77.8°. This gives the complex nominal  $C_{2h}$  symmetry. A search of the Cambridge Structural Database indicates that among  $[Rh_2L_4(\mu-XR)_2]$  complexes, where L = CO,  $PR_3$  and X = O, S, the only analogous structures contain bridging oxygen atoms. Complex 6 possesses all of the features that, stated above, favor a bent structure. Like the other members of the series under study, its sulfur bridges, rhodium centers, and terminal dippe ligands should result in it having bent geometry. Consequently, its planar-anti geometry in the solid state may be due to packing effects.<sup>1</sup>



Fig. 6. ORTEP drawing of  $[Rh(dippe)(\mu-SC_6H_5)]_2$  (6). Ellipsoids are shown at the 30% probability level. All hydrogen atoms are omitted for clarity.

In addition to packing effects, it is possible that 6 is planar as a result of the withdrawal of electron density away from the sulfur atoms into the phenyl groups via lone pair to  $\pi^*$  orbital delocalization, which would attenuate their  $\sigma$ -donating ability. This, in turn, would destabilize the bent conformations. This is the argument that has been put forward by Golen and coworkers in explaining the observed geometrical differences between certain dipalladium µ-arylthiolato and µ-alkylthiolato complexes. They noted that cis-[Pd<sub>2</sub>Cl<sub>2</sub>( $\mu$ -Cl)( $\mu$ -SMe)  $(PMe_3)_2$  and *cis*- $[Pd_2Cl_2(\mu-Cl)(\mu-SCMe_3)(PMe_3)_2]$  exist as bent molecules while cis-[Pd<sub>2</sub>Cl<sub>2</sub>( $\mu$ -Cl)( $\mu$ -SPh)  $(PMe_3)_2$ ], trans- $[Pd_2Cl_2(\mu$ -SPh)\_2(PEt\_3)\_2], and trans- $[Pd_2(SC_6F_5)(\mu-SC_6F_5)_2(PPh_3)_2]$  are found to be planar. Moreover, they point out that the Pd-S distances in cis- $[Pd_2Cl_2(\mu-Cl)(\mu-SPh)(PMe_3)_2]$  are on average about 0.033 and 0.045 Å longer than they are in cis-[Pd<sub>2</sub>Cl<sub>2</sub>( $\mu$ - $Cl(\mu-SMe)(PMe_3)_2$  and  $cis-[Pd_2Cl_2(\mu-Cl)(\mu-SCMe_3)]$ (PMe<sub>3</sub>)<sub>2</sub>], respectively [26]. Yet, a significant increase in Rh–S distance in going from 6 to 3 is absent; it is only about 0.003 A longer in the former than it is in the latter. Structural data simply fails to support the notion that 6 assumes planar geometry as a result of the withdrawal of electron density from the bridging sulfur atoms by the phenyl groups.

Lledós and coworkers [1] point out that a consequence of the quasi invariance of  $\sum$  is that there is an indirect relationship between the hinge angle  $\theta$  and the angle of displacement  $\tau$  of the thiolato substituents from the S–S axis. Complexes **3–6** bear this out. After taking into account the geometrical constraints and steric effects that are imposed by the thiolate substituents, there is a general trend of decreasing  $\tau$  as  $\theta$  becomes larger. For example, compare the values of **4** to those of **6**. The former complex has a of 126.3° and a  $\tau$  of 85.8° while the latter complex has values of 180° and 77.8°, respectively.

# 3.2. Dynamic NMR spectra of $[Rh(dippe)(\mu-SR)]_2$ complexes

All members of the series of  $[Rh(dippe)(\mu-SR)]_2$ complexes in this study are fluxional on the NMR timescale when they are in solution. In this respect, they resemble  $[Ni(dippe)(\mu-S)]_2$ ,  $[Ni_2(dippe)_2(\mu-S)(\mu-SR)]^+$ ,  $[Ni(dippe)(\mu-SCH_3)]_2^{2+}$ , and other sulfur-bridged transition metal complexes that have been reported in the literature [16]. Yet, the variable temperature <sup>1</sup>H and <sup>31</sup>P NMR spectra of  $[Rh(dippe)(\mu-SR)]_2$  complexes neither are uniform as a group nor do they differ from each other in a manner that can be predicted from the structural data.

It is worthwhile to consider what one would expect to see in the <sup>31</sup>P NMR spectra of the complexes. In both bent *syn-exo* and *syn-endo* compounds, all phosphorus nuclei are equivalent and therefore a single doublet (due to Rh–P coupling,  $J \approx 170$  Hz) should be seen for each isomer present. In the bent-anti structure, however, there are two different types of phosphorus and therefore two separate resonances are expected, each a doublet of doublets ( $J_{\text{Rh-P}} \approx 170 \text{ Hz}$ ,  $J_{\text{P-P}} \approx 20 \text{ Hz}$ ). If the bent syn-exo or syn-endo structures undergo a rapid ring-inversion process, then the two isomers interconvert and a single type of phosphorus (doublet) should be observed. In the bent-anti structures, ring inversion will interchange the two types of phosphorus nuclei, rendering them equivalent. A simple doublet will be observed. Consequently, the observation of simple doublets (due to  $J_{Rh-P}$ ) does not tell much about the structure(s) present. In addition, sulfur inversion can interconvert syn and anti structures as shown in Scheme 1, resulting in interchange of all three isomers. If all of these dynamic processes are occurring, then a solution containing a mixture of all three structures might display a single doublet for all of them!

Similar arguments can be made concerning the dippe methyl groups in the <sup>1</sup>H NMR spectrum. The syn-exo and syn-endo structures each have two different kinds of diisopropyl group, those pointing into the 'pocket' created by the bent structure, and those pointing away from the pocket. Since the methyl groups on each isopropyl are also inequivalent, this means that four types of methyl are expected for each of these isomers. If the structure is fluxional due to ring inversion, then the synexo and syn-endo isomers are interconverting. However, the two types of isopropyl group in one isomer interconvert with the two types of isopropyl group in the other isomer, but in a pairwise fashion, and therefore one expects there will still be two types of isopropyl group in the time-averaged spectrum, each with two distinct methyl resonances. In the less symmetrical bentanti structure, all four isopropyl groups are distinct so that eight types of methyl are to be observed in the static molecule. If the bent-anti structure undergoes rapid ring-inversion, then two types of isopropyl group will be observed, again because of a pairwise correlation in the exchange. This would result in four distinct types of methyl groups. Should sulfur inversion be occurring in any of these complexes, then all isopropyl groups will be rendered equivalent, and only two types of methyl will be seen.

#### 3.3. Dynamic NMR spectra of $[Rh(dippe)(\mu-SH)]_2$

The conformations that 1 adopts in solution are most likely limited to the bent form(s) as seen in the X-ray structure, and variable temperature NMR spectra are consistent with this. Evidence for the fluxionality of 1 is provided by the signals of the dippe isopropyl substituents in the <sup>1</sup>H NMR spectrum and the phosphorus in the <sup>31</sup>P NMR spectra.

The <sup>1</sup>H NMR spectrum of **1** at room temperature displays only two types of methyl group, each a doublet

of doublets due to coupling to the methine H and the phosphorus. Only two sets of doublets of doublets are observed from 50 to 10 °C. As the temperature is lowered to -105 °C, all proton signals show broadening, which prevents clear identification of separate isopropyl methyl resonances. However, no sign of coalescence is indicated.

The <sup>31</sup>P NMR spectra of **1** between 20 and -100 °C in THF-d<sub>8</sub> are shown in Fig. 7. The spectrum at 20 °C consists of a doublet at  $\delta$  93.16. As the temperature is lowered to -80 °C, that doublet broadens and then resolves into two doublets, with one being twice the intensity of the other. Both upfield and downfield signals have nearly identical phosphorus–rhodium coupling constants of 176.2 and 176.6 Hz, respectively. Lowering the temperature still further to -105 °C results in slight broadening of the two doublets, but solvent-imposed limitations prevented further cooling.

When this same experiment is conducted in toluene- $d_8$ , two doublets are observed that are nearly equal in intensity. A reasonable scenario, is that at 20 °C, both ring inversion and sulfur inversion are quite energetically accessible and the two processes allow 1 to interconvert among all of its bent forms in a manner that is shown in Scheme 1. As the temperature is lowered, sulfur inversion is slowed, so that bent-anti and bent-syn structures no longer rapidly interconvert. However, ring inversion is still rapid (as seen in other systems [8]) so that the interconverting syn-exo and syn-endo complexes display one doublet, whereas the two interconverting (but equivalent) bent-anti structures display a second doublet. As the Xray structure shows the syn-endo structure, it appears likely that the bent-anti isomer corresponds to the lower intensity signal in the THF-d<sub>8</sub> <sup>31</sup>P NMR spectrum. Changing to toluene-d<sub>8</sub> lowers the ground state energy of the bent-anti isomer. Therefore, a larger percentage of the population of 1 is "stranded" as the bent-anti isomer.



Fig. 7. <sup>31</sup>P NMR spectra of 1 in THF-d<sub>8</sub> from +20 to -100 °C.

Further evidence for the above hypothesis comes from examination of the dynamic spectra of 2.

#### 3.4. Dynamic NMR spectra of $[Rh(dippe)(\mu-SMe)]_2$

The <sup>1</sup>H NMR spectra of **2** in THF-d<sub>8</sub> show evidence for at least two types of isopropyl methyl group, but as before, broadening at low temperature prevents definitive assignment of the number of species present. At +50 °C, however, the dippe methyl resonances clearly appear more complex than four simple doublets of doublets, suggesting that more than two types of isopropyl group are present.

The <sup>31</sup>P NMR spectra of **2** in THF-d<sub>8</sub> at temperatures from 60 to -100 °C are shown in Fig. 8. At the highest temperature measured, the spectrum consists of a sharp doublet, with  $J_{P-Rh} = 172.6$  Hz, that is centered at  $\delta$ 90.80. With decreasing temperature, the doublet shifts slightly upfield and broadens. At -70 °C, it coalesces to a broad singlet and further cooling to -100 °C causes the signal to sharpen into a pair of doublets of doublets with  $J_{P-Rh} = 172.0$  Hz and  $J_{P-P} = 21.8$  Hz. This pattern is consistent with a static bent-*anti* geometry for **2** as observed in the solid state X-ray structure. The <sup>31</sup>P NMR data indicate that ring inversion occurs as the temperature is raised, equilibrating the two types of phosphorus but producing none of the *syn* isomers.

# 3.5. Dynamic NMR spectra of $[Rh(dippe)(\mu-SCy)]_2$

The <sup>1</sup>H NMR spectrum of complex **3** in THF-d<sub>8</sub> lacks fine structure for all temperatures at which it was measured. From 60 to -60 °C nearly all signals appear as broad singlets, suggesting that fluxional behavior is responsible for the broadness. At RT, the methyl protons of the isopropyl substituents give rise to two doublets of doublets. Based on this data, it appears that **3** is interconverting among several isomers by either one or more processes like the other bent [Rh(dippe)( $\mu$ -SR)]<sub>2</sub>



Fig. 8. <sup>31</sup>P NMR spectra of 2 in THF-d<sub>8</sub> from +60 to -100 °C.

complexes in the series. Unfortunately, the <sup>31</sup>P NMR spectra of **3** in THF-d<sub>8</sub> fail to provide insight into what those processes are since coalescence is never observed. The spectra all display a single doublet that is centered at approximately  $\delta$  82.7, which does broaden slightly at about -105 °C (Fig. 9).

# 3.6. Dynamic NMR spectra of $[Rh(dippe)(\mu-S-biphe-nyl)]_2$

As with the other compounds, the <sup>1</sup>H NMR spectrum of complex **4** in toluene- $d_8$  lacks detailed structure at most temperatures at which it was measured. However, while at +85 °C two doublets of doublets are seen, these resonances coalesce and then separate as four broad singlets at 20 °C.

The <sup>31</sup>P NMR spectra vary considerably with temperature (Fig. 10). At 90 °C, **4** produces a sharp doublet that is centered at 91.41 with a  $J_{(P-Rh)} = 180.3$  Hz. This signal broadens as the temperature is lowered, and at 50 °C it coalesces to a broad singlet at  $\delta$  90.65. This singlet then sharpens to yield two sharp doublets that, at 20 °C, are centered at  $\delta$  91.22 and 89.02, with the upfield signal being approximately twice the intensity of the downfield signal. Furthermore, both doublets have the same phosphorus–rhodium coupling constant of  $J_{(P-Rh)} =$ 178.5 Hz. When the temperature is decreased below 20 °C, the upfield doublet begins to broaden as the downfield doublet remains sharp. Moreover, the ratio be-



Fig. 9. <sup>31</sup>P NMR spectra of 3 in THF-d<sub>8</sub> from +60 to -105 °C.



Fig. 10. <sup>31</sup>P NMR spectra of 4 in toluene-d<sub>8</sub> from +90 to -75 °C.

tween the two signals changes; at 0 °C it is 1:4, and at lower temperatures the ratio is ~1:20. A second coalescence of the larger of the doublets occurs at -25 °C to produce a broad singlet at 88.39. This singlet begins to resolve as the temperature is lowered further, and at -75 °C it becomes a pair of doublets of doublets with  $J_{(P-P)} = 19.8$  Hz and  $J_{(P-Rh)} = 177.0$  Hz.

The <sup>31</sup>P NMR data suggest that both ring and sulfur inversion processes are slowed in 4 as the temperature is lowered from +90 to -75 °C. There is only one doublet at the high temperature limit because both processes are facile. 4 is interconverting among all of its isomers rapidly enough to render equivalent all phosphorus atoms. However, sulfur inversion begins to slow as the temperature is lowered so that, at 20 °C, the population of 4 is clearly distributed between bent-syn and bent-anti isomers, with the latter corresponding to the more intense upfield doublet. Ring inversion is still very fast, and so that the phosphorus atoms in the bent-anti isomer are equivalent, giving a doublet, and the syn-exo and synendo isomers rapidly interconvert, giving a doublet as observed in 1. Ring inversion slows and eventually shuts down (on the NMR timescale) in the bent-anti isomer, producing a pair of doublets of doublets at -75 °C. The slowing down of ring inversion should also allow the synexo and syn-endo isomers of 4 to be resolved, but the process is still too rapid at low temperature to result in anything other than broadening. The fact that the ratio of bent-anti to bent-syn isomers becomes larger as the temperature is lowered indicates that the former geometry is the most stable in solution. This runs counter to what would be predicted based on the X-ray crystallographic result. Moreover, it makes it harder to rationalize the bent-exo geometries of 3 and 4 in the solid state. The <sup>31</sup>P NMR data are in agreement with the preference for the bent-anti structure in 2 at low temperature.

#### 3.7. Dynamic NMR spectra of $Rh_2(dippe)_2(\mu$ -SPh)

The <sup>1</sup>H and <sup>31</sup>P NMR data for the planar complex **6** indicate that it undergoes sulfur inversion throughout the measured temperature range, which extends from 60 to -105 °C. All proton spectra that were obtained during variable temperature experiments are broad.

The <sup>31</sup>P NMR spectrum of **6** in THF-d<sub>8</sub> broadens upon lowering the temperature from 25 to -105 °C as shown in Fig. 11. Collapse of the doublet that is initially centered at  $\delta$  89.48 leads to formation of two broad doublets that are centered at 90.29 and 86.51. Here, the downfield signal is approximately 2.5 times as intense as the upfield signal.

The <sup>31</sup>P NMR spectral data are consistent with the presence of both bent-*anti* and bent-*syn* isomers for **6** in solution (or possibly planar-anti and planar-syn) and that these isomers are involved in an equilibrium as observed in **4**. It is assumed that the more intense



Fig. 11. <sup>31</sup>P NMR spectra of **6** in toluene-d<sub>8</sub> from +90 to -75 °C.

downfield doublet corresponds to the bent-*anti* isomer. Similar equilibria have been observed for  $[Pt_2(\mu-SC_6F_5)_2(SC_6F_5)_4]^{2+}$ ,  $[Pt_2(\mu-p-SC_6HF_4)_2(p-SC_6HF_4)_4]^{2+}$ , and  $[Pt_2(\mu-p-SC_6F_4(CF_3))_2(p-SC_6F_4(CF_3))_4]^{2+}$  [17]. Interestingly, Torrens and coworkers reported that the NMR data for  $[Rh(\mu-SC_6HF_4)(COD)]_2$ ,  $[Rh(\mu-SC_6H_4F)(COD)]_2$ ,  $[Rh(\mu-SC_6H_4F)(COD)]_2$ , and  $[Rh(\mu-SCF_3)(COD)]_2$  indicate that these complexes most likely adopt a rigid *syn* structure in solution, while the data suggest that  $[Rh(\mu-SC_6HF_4)(CO)]_2$  and  $[Rh(\mu-SC_6H_4F)(CO)]_2$  are fluxional [24]. It is possible that the replacement of COD with CO is responsible for the change in behavior.

The free energy of activation  $(\Delta G_{ri}^{I})$  for the ring inversion process was calculated for 2 and 4, and the free energy of activation for the sulfur inversion process  $(\Delta G_{\rm si}^{\ddagger})$  was calculated for 1, 4, and 6 at their coalescence temperatures.<sup>4</sup> These values are listed in Table 3. Ring inversion values for **2** and **4** are 16.5 and 19.7 kJ mol<sup>-1</sup>, respectively. These values are in agreement with the conclusion of two previous studies, namely, that  $\Delta G^{\ddagger}$  for ring inversion in bent M<sub>2</sub>X<sub>2</sub> complexes is always less than 35 kJ mol<sup>-1</sup> [27]. Sulfur inversion values for 1, 4, and 6 are 42.5, 61.4, and 32.1 kJ mol<sup>-1</sup>, respectively. These compare favorably with what Torrens and coworkers [17] report for the polyfluorinated benzenethiolate-bridged platinum dimers that are cited above, and with the values that Killops and Knox [5] report for  $\mu$ thio-bis[carbonyl(n-cyclopentadienyl)ruthenium] complexes (Scheme 2).

<sup>&</sup>lt;sup>4</sup> From the separation of the resonances ( $\Delta v$ ) in the low temperature limit,  $k = \pi \Delta v / 2^{1/2}$ .

Table 3 Free energy of activation  $\Delta G^{\ddagger}$  for ring inversion and sulfur inversion

Complex	Solvent	$\Delta G^{\ddagger}$ ring inversion (kJ mol <sup>-1</sup> )	$\Delta G^{\ddagger}$ sulfur inversion (kJ mol <sup>-1</sup> )
$[Rh(dippe)-(\mu-SH)]_2$ (1)	THF-d <sub>8</sub>		42.5
$[Rh(dippe)-(\mu-SCH_3)]_2$ (2)	toluene-d <sub>8</sub>	16.5	
$[Rh(dippe)-(\mu-SC_{12}H_9)]_2$ (4)	toluene-d <sub>8</sub>	19.7	61.4
$[Rh(dippe)-(\mu-SC_6H_5)]_2$ (6)	THF-d <sub>8</sub>		32.1

#### 4. Conclusion

With the exception of **6**,  $[Rh(dippe)(\mu-SR)]_2$  complexes exhibit a bent geometry in the solid state. However, the orientation of the bridging sulfur substituents changes as their steric bulk increases, presumably to attenuate both ligand-substituent and substituent-substituent interactions. It is unclear why **6** has a planar*anti* geometry in the solid state, although as pointed out by Lledós and coworkers [1], the energy difference between these isomers is quite small. Nonetheless, along with complexes **3–5**, it demonstrates the indirect relationship between  $\theta$  and  $\tau$  in molecules that have an  $M_2(SR)_2$  core.

While the <sup>1</sup>H and <sup>31</sup>P NMR spectra of [Rh(dippe)( $\mu$ -SR)]<sub>2</sub> complexes are somewhat dissimilar, they do indicate that both ring inversion and sulfur inversion occurs in the members of this series. Consequently, they can access several isomeric forms when they are in solution. Sulfur inversion appears to have a larger barrier than ring inversion and can be more easily frozen out. From these studies, it is concluded that X-ray studies have little predictive value upon the structure(s) adopted in solution. Lastly, <sup>31</sup>P NMR spectroscopy in toluene-d<sub>8</sub> and THF-d<sub>8</sub> suggests that sulfur inversion in **1**, **4**, and **6** operates according to a non-dissociative mechanism, as coordinating solvent does not affect the rate of the process.

#### 5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publications nos. CCDC-222639–222644. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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