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Oxidative Addition of Benzenethiol to $[Rh(PMe_3)_4]Cl$ Giving Cationic and Neutral Hydrido(benzenethiolato)rhodium(III) Complexes

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$[Rh(PMe_3)_4]Cl$ reacts with HSPh to give cationic hydrido(benzenethiolato)rhodium complex, *cis*-$[RhH(SPh)(PMe_3)_4]Cl$ (**1**). The NMR (^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$) spectra as well as elemental analyses of **1** indicate the octahedral coordination with a hydrido and an SPh ligand at mutually cis positions. Reaction of $[Rh(PMe_3)_4]Cl$ with HSPh in the presence of NEt_3 gives a mixture of *mer*-$RhCl(H)(SPh)(PMe_3)_3$ (**2**) (38%) and $[Rh_2(\mu\text{-}SPh)_2(PMe_3)_4]$ (**3**) (<20%). X-Ray crystallography has revealed the molecular structure of **2**, which has slightly distorted octahedral coordination around the Rh center with three PMe_3 ligands at meridional coordination sites. The hydrido ligand, which is at a distance of 1.52 Å from the Rh center, is at trans position to Cl and cis position to the SPh ligand. Complex **1** reacts with equimolar MeI to give MeSPh in 86% yield.

Oxidative addition of H–S bond of thiol to low valent transition metal complexes is a common synthetic method of hydrido(thiolato)metal complexes under mild conditions.[1—8] Although hydrido(thiolato)rhodium(III) complexes having tertiary phosphine ligands were obtained by the reaction of thiols with chloro- and thiolatorhodium(I) complexes, there have been few reports on the reaction of thiols with cationic Rh(I) phosphine complexes to give oxidative addition products. Here we report the reaction of $[Rh(PMe_3)_4]Cl$ with thiophenol in the absence or presence of NEt_3 to give cationic or neutral hydrido(benzenethiolato)rhodium(III) complexes, as well as spectroscopic and crystallographic results of the complexes.

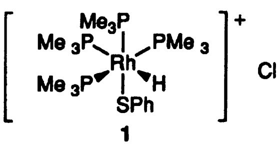
Results and Discussion

Reaction of $[Rh(PMe_3)_4]Cl$ with HSPh. $[Rh(PMe_3)_4]Cl$ reacts with equimolar HSPh at room temperature in THF to cause precipitation of a pale yellow solid.

$$[Rh(PMe_3)_4]Cl + HSPh \longrightarrow cis\text{-}[Rh(H)(SPh)(PMe_3)_4]Cl \qquad (1)$$

Recrystallization of the solid from acetone gives *cis*-$[RhH(SPh)(PMe_3)_4]Cl$ (**1**) as orange air sensitive crystals in 52% yield. The following spectroscopic results of **1**, as well as elemental analyses agree well with the structure in Scheme 1.

The IR spectrum of **1** shows a strong peak at 1982 cm^{-1} due to ν(Rh–H) vibration. The ^1H NMR spectrum shows signals due to PMe_3 hydrogens as an apparent triplet due to virtual coupling at 1.56 ppm[9] and two doublets at 1.73 and 1.50 ppm (^1J(PH) 9 and 7 Hz, respectively). The former signal is assigned to hydrogens of two equivalent PMe_3 ligands at mutually trans positions and the latter to two other PMe_3 ligands, respectively. The hydrido signal is observed as a multiplet at −9.93 ppm, and shows a much larger ^2J(PH) coupling constant (171 Hz) than the other ^2J(PH) and ^1J(RhH) values (13—21 Hz). The hydrido signal in ^1H NMR spectrum of *cis,mer*-$RhH(SPh)_2(PMe_3)_3$ was reported to show a similarly large ^2J(PH) value (180 Hz) that is assigned unambiguously to coupling of the hydride with trans phosphorus nucleus based on the ^{31}P NMR spectra under selective ^1H decoupling conditions. The results indicate the structure of **1** with hydrido and thiolato ligands at mutually cis positions rather than trans structure. The $^{13}C\{^1H\}$ NMR spectrum of **1** shows signals due to the PMe_3 carbons as two doublets and an apparent triplet due to virtual coupling. Doublet signals at 143.7 and 130.5 ppm are assigned to a phenyl carbon atom bonded to sulfur and those at ortho positions, respectively. Splitting of the signals due to Rh–C or P–C coupling indicates that the thiolato ligand does not undergo dissociation in the solution. The $^{31}P\{^1H\}$ NMR spectrum of **1** shows three peaks in a 1 : 2 : 1 peak area ratio, and the peak pattern is consistent with an AB_2CX system. All these results support the proposed structure for **1**. Preliminary crystallographic results of **1** also agree with the cationic structure with hydrido and thiolato ligands at mutually cis positions.[10]



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Scheme 1.

Reaction of $[Rh(PMe_3)_4]Cl$ with HSPh in the Presence of NEt_3. $[Rh(PMe_3)_4]Cl$ reacts with HSPh in the presence of NEt_3 to give a mixture of THF soluble orange crystals (38% yield) and a smaller amount of THF insoluble white solid. The products are separated from each other by fractional crystallization. The former product was determined as *mer*-$RhCl(H)(SPh)(PMe_3)_3$ (**2**) based on the crystallographic results as well as the NMR spectra. Added NEt_3 seems to promote elimination of the PMe_3 ligand before or after oxidative addition of the thiol.

$$[\mathrm{Rh(PMe_3)_4}]\mathrm{Cl} + \mathrm{HSPh} \xrightarrow{+\mathrm{NEt_3}} \underset{\mathbf{2}}{mer\text{-}[\mathrm{RhCl(H)(SPh)(PMe_3)_3}]} + \underset{\mathbf{3}}{[\mathrm{Rh_2(\mu\text{-}SPh)_2(PMe_3)_4}]} \quad (2)$$

Figure 1 shows the molecular structure of **2** obtained by X-ray crystallography. Selected bond lengths and angles are summarized in Table 1. The molecule has a slightly distored octahedral coordination around the rhodium center. The hydrido ligand is located at 1.52 Å from the rhodium atom in the final D map. Rh–Cl and Rh–S bond distances are 2.500(1) and 2.418(1) Å, respectively, and are similar to those of already reported chloro and thiolato Rh(III) complexes.[4,5,11] The PMe_3 ligands occupy three meridional coordination sites with Rh–P bond lengths in the range 2.29—2.34 Å.

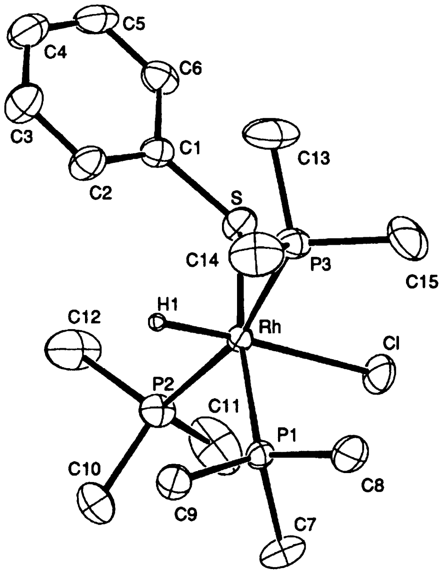


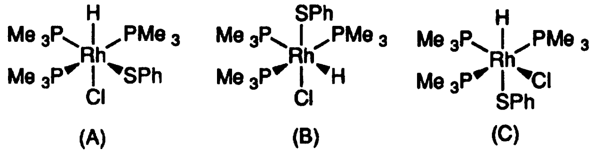
Fig. 1. Molecular structure of complex **2** by X-ray crystallography.

Table 1. Selected Bond Distances and Angles of **2**

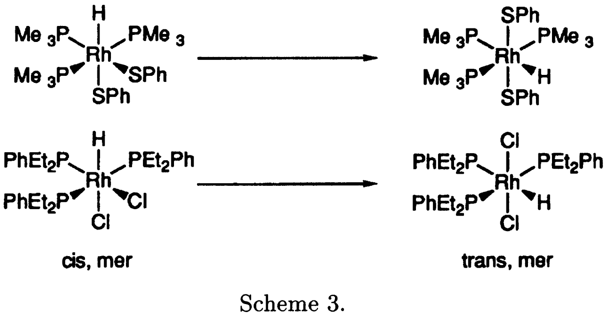
	Distances (Å)		
Rh–Cl	2.500(1)	Rh–S	2.418(1)
Rh–P1	2.296(1)	Rh–P2	2.336(1)
Rh–P3	2.329(1)	S–C1	1.756(3)
C1–C2	1.385(5)	C2–C3	1.395(5)
C3–C4	1.359(6)	C4–C5	1.358(6)
C5–C6	1.383(5)	C1–C6	1.394(5)
P1–C7	1.820(4)	P1–C8	1.811(4)
P1–C9	1.808(4)	P2–C10	1.813(4)
P2–C11	1.791(4)	P2–C12	1.807(4)
P3–C13	1.801(4)	P3–C14	1.809(5)
P3–C15	1.821(4)	Rh–H1	1.52(3)
	Angles (deg)		
S–Rh–P1	170.56(3)	S–Rh–P2	85.52(3)
S–Rh–P3	87.68(3)	Cl–Rh–P1	85.88(3)
Cl–Rh–P2	96.36(4)	Cl–Rh–P3	95.74(4)
P1–Rh–P2	94.36(4)	P2–Rh–P3	165.51(4)
P1–Rh–P3	94.44(3)	H1–Rh–P1	89.(1)
H1–Rh–P2	85.(1)	H1–Rh–P3	83.(1)
H1–Rh–S	100.(1)	H1–Rh–Cl	175.(1)
Rh–S–C1	115.4(1)	S–C1–C2	125.1(3)
S–C1–C6	118.7(3)	C2–C1–C6	116.2(3)
C1–C2–C3	121.0(4)	C2–C3–C4	121.4(4)
C3–C4–C5	118.6(4)	C4–C5–C6	121.0(4)
C1–C6–C5	121.8(4)		

cis,mer-$RhH(SPh)_2(PMe_3)_3$ having two thiolato ligands at mutually cis positions was reported to undergo facile isomerization in solutions into thermodynamically more stable *trans,mer*-$RhH(SPh)_2(PMe_3)_3$.[4b,c] Oxidative addition of HCl to a Wilkinson type complex, $RhCl(PEt_2Ph)_3$, was reported to give *cis,mer*- and *trans,mer*-$RhHCl_2(PEt_2Ph)_3$ as the kinetic and thermodynamic products, respectively.[11,12] These observations suggest that complex **2**, which has the structure (A) in Scheme 2, is thermodynamically less stable than the other structure (B). Isomerization similar to Scheme 3 would cause a structural change of **2** from (A) into (B). The NMR spectra of **2** were measured in order to see whether it undergoes isomerization in solutions.

The ${}^1H$ NMR spectrum of **2** in CD_2Cl_2 shows a hydrido signal at −17.6 ppm. ${}^2J(\mathrm{PH})$ and ${}^1J(\mathrm{RhH})$ coupling constants are all 18 Hz, indicating that no PMe_3 ligand exists at trans position of the hydrido ligand. Figure 2 shows the ${}^{31}P\{{}^1H\}$ NMR spectrum of **2**, as well as the computer simulated spectrum based on the assumption of an AB_2X spin system. The obtained J(PP)(30 Hz) and J(RhP)(104 and 94 Hz) values agree with those of analogous Rh(III) complexes.[4,5,11,12] These NMR results indicate that complex **2** in solution has the hydrido ligand at cis position to each of three PMe_3 ligands, and agree with the structure (A) in Scheme 2 rather than (B). Structure (C), which is also consistent with the NMR spectra, is not plausible as the structure of **2** in the solution, because the ${}^1H$ NMR signals obtained soon after preparation of the solution by dissolving the single crystals do not undergo any change at all after keeping the solution at room temperature for 24 h or even after



Scheme 2.



Scheme 3.

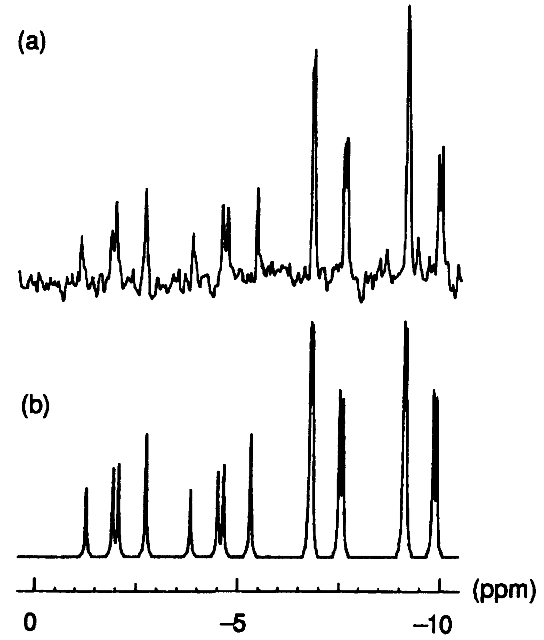
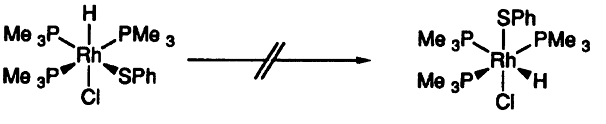
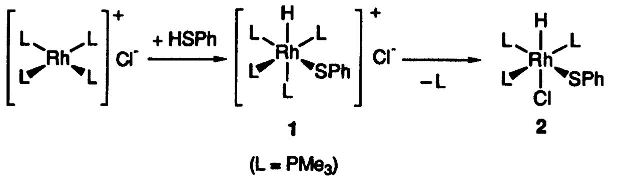


Fig. 2. (a) Observed ^{31}P{^{1}H} NMR spectra of **2** and (b) the calculated spectra based on assumption of an AB$_2$X pattern.



Scheme 4.



Scheme 5.

heating the solution at 40 °C for 4 h. These results indicate that complex **2** has structure (A) both in the solid state and in the solutions and that it does not undergo a structural change from (A) into (B) under the conditions (Scheme 4).

Scheme 5 shows a possible pathway for formation of **2** in reaction (2) involving initial formation of **1**, which undergoes ensuing substitution of a PMe$_3$ ligand by chloride to give **2**. Since the PMe$_3$ ligand at trans position to hydrido in **1** is most labile, the formation of **2** with hydrido and thiolato ligands at mutually trans positions is consistent with the reaction pathway.

Reaction (2) gives a small amount of THF insoluble white solid also. The ^{1}H NMR spectrum of the by-product shows signals due to phenyl hydrogens and PMe$_3$ hydrogens in a 5 : 18 peak area ratio. The latter signal appears as a filled-in doublet which is often observed in complexes containing PMe$_3$ ligands at a mutually cis positions.[13] The results as well as the ^{31}P{^{1}H} NMR spectrum showing a simple doublet at 3.4 ppm (J(RhP)=113 Hz) indicate the structure, [Rh$_2$(μ-SPh)$_2$(PMe$_3$)$_4$] (**3**), whose analogues with other phosphine ligands have been prepared and well characterized.[14—17] Reactions of mixtures of thiol and tertiary amine with chlorotransition metal complexes were also reported to provide the corresponding thiolato complexes accompanied by the formation of trialkylammonium chloride.[18]

Reaction of 1 with MeI. Complex **1** reacts with equimolar MeI to give MeSPh (86%) which is identified by GC analysis of the reaction mixture. The ^{1}H NMR spectrum of the reaction mixture in CD$_2$Cl$_2$ shows no indication of formation of methane. The results indicate that thiolato ligand reacts more easily with MeI than the hydrido ligand. Ethylpalladium thiolato complex, *trans*-PdEt(SAr)(PEt$_3$)$_2$, was also reported to react with organic halides such as MeI, PhCH$_2$Br, and CH$_2$=CHCH$_2$Cl to give the corresponding organic sulfides through C–S bond formation.[19] Since reaction of **1** with excess MeI (>10 equiv) gives MeSPh in lower yield (<40%) due to other reactions, determination of rate constant of the reaction under pseudo-first-order conditions was not successful.

Experimental

General, Materials, and Measurements. All the manipulations of the complexes were carried out under nitrogen or argon using Schlenk technique. Solvents were dried in the usual manners, distilled and stored under nitrogen atmosphere. [Rh(PMe$_3$)$_4$]Cl was prepared according to the literature.[20] IR spectra were measured on a JASCO 810 spectrophotometer. NMR spectra (^{1}H, ^{13}C, and ^{31}P) were recorded on a JEOL FX-100 spectrometer. Elemental analyses were carried out by Yanagimoto Type MT-2 CHN autocorder.

Reaction of [Rh(PMe$_3$)$_4$]Cl with Thiophenol. To [Rh(PMe$_3$)$_4$]Cl (560 mg, 1.3 mmol) dispersed in THF (30 cm^3) was slowly added HSPh (140 mg, 1.3 mmol) at room temperature. Stirring the mixture for 10 h caused the precipitation of a pale yellow solid which was filtered and washed with Et$_2$O several times. Recrystallization of the solid product from acetone (20 cm^3) gave [RhH(SPh)-(PMe$_3$)$_4$]Cl (**1**) as orange plates (370 mg, 52%). Mp: 138—142 °C (decomp). Anal. Calcd for C$_{18}$H$_{42}$ClP$_4$RhS: C, 39.1; H, 7.7%. Found: C, 39.1; H, 7.6%. ^{1}H NMR (100 MHz in CD$_2$Cl$_2$ at −40 °C) δ=7.6—7.4 (m, C$_6$H$_5$, 2H), 7.1—6.8 (m, C$_6$H$_5$, 3H), 1.73 [d, J(PH)=9 Hz, P(CH$_3$)$_3$, 9H], 1.56 [apparent triplet due to virtual coupling, P(CH$_3$)$_3$, 18H], 1.50 [d, J(PH)=7 Hz, P(CH$_3$)$_3$, 9H], −9.93 [ddddd, J(PH) or J(RhH)=171, 21, 21, 16, 13 Hz, Rh–H]. ^{31}P{^{1}H} NMR (from external 85% H$_3$PO$_4$, 40 MHz in CD$_2$Cl$_2$ at −40 °C) δ=−10.1 [dddd, J(RhP)=71 Hz, J(PP)=29, 28, 28 Hz, 1P], −14.0 [ddd, J(RhP)=90 Hz, J(PP)=28, 28 Hz, 2P], −31.4 [dddd, J(RhP)=79 Hz, J(PP)=28, 28, 28 Hz, 1P]. ^{13}C{^{1}H} NMR (25 MHz in CD$_2$Cl$_2$ at −40 °C) δ=143.7 [d, J(RhC) or J(PC)=11 Hz, S–C], 130.5 [d, J(RhC) or J(PC)=4 Hz, ortho], 128.3 [s, meta], 122.7 [s, para], 24.0 [d, J(PC)=31 Hz, P(CH$_3$)$_3$], 20.9 [apparent triplet due to virtual coupling, J(PC)=31 Hz, P(CH$_3$)$_3$], 18.3 [d, J(PC)=24

Table 2. Atomic Coordinates and B_{eq} or B_{iso} of **2**

Atom	x	y	z	B_{eq} (or B_{iso})
Rh	0.16483(1)	0.09405(1)	0.24227(1)	2.46
Cl	0.26571(5)	0.00453(6)	0.29270(7)	4.88
S	0.15587(5)	0.12276(5)	0.41094(6)	3.96
P1	0.19032(5)	0.05521(4)	0.08907(5)	2.95
P2	0.24307(5)	0.19879(5)	0.23293(6)	3.80
P3	0.06426(5)	0.01175(5)	0.26374(7)	3.89
C1	0.0812(2)	0.1823(2)	0.4432(2)	3.4
C2	0.0365(2)	0.2218(2)	0.3795(3)	4.3
C3	−0.0208(2)	0.2690(2)	0.4119(3)	5.4
C4	−0.0352(3)	0.2776(3)	0.5068(3)	5.5
C5	0.0079(2)	0.2393(2)	0.5705(3)	5.2
C6	0.0646(2)	0.1917(2)	0.5399(3)	4.2
C7	0.2891(2)	0.0604(2)	0.0526(3)	5.2
C8	0.1748(2)	−0.0422(2)	0.0613(3)	5.3
C9	0.1395(2)	0.1022(2)	−0.0057(2)	4.3
C10	0.2631(2)	0.2438(2)	0.1196(3)	5.5
C11	0.3352(3)	0.1848(3)	0.2834(4)	8.4
C12	0.2086(4)	0.2799(2)	0.2960(4)	9.5
C13	0.0004(3)	0.0293(3)	0.3616(4)	7.7
C14	−0.0041(2)	0.0057(3)	0.1676(4)	7.2
C15	0.0900(3)	−0.0844(2)	0.2898(4)	6.8
H1	0.103(2)	0.145(2)	0.202(2)	3.6[a]

a) B_{iso}.

Hz, $P(CH_3)_3$].

Reaction of $[Rh(PMe_3)_4]Cl$ with Thiophenol in the Presence of NEt_3. To $[Rh(PMe_3)_4]Cl$ (170 mg, 0.38 mmol) disperesed in THF (30 cm^3) was added NEt_3 (40 mg, 0.39 mmol) and then HSPh (42 mg, 0.38 mmol) at room temperature. Stirring the mixture for 12 h caused the precipitation of a white solid. After removal of the solid by filtration, the filtrate was evaporated to dryness, and the remaining red oil was stirred with Et_2O (2 cm^3) to give *mer*-$RhCl(H)(SPh)(PMe_3)_3$ (**2**) as an orange brown solid (68 mg, 38%). Anal. Calcd for $C_{15}H_{33}ClP_3RhS$: C, 37.8; H, 7.0%. Found: C, 37.1; H, 6.4%. ^{1}H NMR (100 MHz in CD_2Cl_2 at −40 °C) δ=7.7—7.4 (m, C_6H_5, 2H), 7.1—6.8 (m, C_6H_5, 3H), 1.60 (d, J(PH)=9 Hz, $P(CH_3)_3$, 9H], 1.48 [apparent triplet due to virtual coupling $P(CH_3)_3$, 18H], −17.6 [dddd, J(PH) or J(RhH)=18, 18, 18, 18 Hz, Rh–H]. $^{31}P\{^1H\}$ NMR (from external 85 % H_3PO_4, 40 MHz in CD_2Cl_2 at room temperature) δ=−4.0 [m, J(RhP)=104 Hz, J(PP)=30 Hz, 1P], −9.0 [m, J(RhP)=94 Hz, 2P]. Mp: 151—154 °C (decomp). The peak positions and coupling constants of $^{31}P\{^1H\}$ NMR spectrum were obtained by comparison with computer-simulated spectra based on the assumption of an AB_2X pattern.

The white solid product, separated from the reaction mixture by filtration, (28 mg) shows a ^{1}H NMR spectrum which agrees with the structure $[Rh_2(\mu\text{-}SPh)_2(PMe_3)_4]$ although the elemental analyses did not give satisfactory results, probably due to contamination with impurities such as triethylammonium chloride. ^{1}H NMR (100 MHz in CD_2Cl_2 at 25 °C) δ=7.1—7.3 (m, 4H, C_6H_5), 6.6—6.8 (m, 6H, C_6H_5), 1.66 [filled-in doublet, 36H, $P(CH_3)_3$]. $^{31}P\{^1H\}$ NMR (from external 85% H_3PO_4, 40 MHz in CD_2Cl_2 at room temperature) 3.4 [d, J(RhP)=113 Hz].

Reaction of 1 with MeI. To a CH_2Cl_2 (2 cm^3) solution of **1** (42 mg, 7.6 μmol) was added MeI (1.2 mg, 8.5 μmol) at room temperature. The reaction mixture was soon turned from orange into dark brown. After stirring for 8 h at the temperature GC measurement of the reaction product by using diphenylmethane as the internal standard showed formation of MeSPh (86%).

Crystal Structure Determination of 2. A crystal of **2** suitable for crystallography was obtained from acetone and mounted in a glass capillary tube under argon.

Crystal Data. $C_{15}H_{32}ClP_3RhS$, M=475.55, orthorhombic, a=17.662(4), b=17.940(6), c=13.976(6) Å, U=4428 Å^3 (by least squares refinement on diffractometer angles for 20 automatically centered reflections, λ=0.71069 Å), space group *Pbca* (no. 61), Z=8, D_c=1.427 g cm^{-3}, F(000)=1960. Yellow air sensitive plates. Crystal dimensions: 0.30×0.55×0.60 mm, μ(Mo $K\alpha$)11.80 cm^{-1}.

Data Collection and Processing. AFC-5R diffractometer, ω scan mode, scan speed 4.0 min^{-1}, graphite monochromated Mo $K\alpha$ radiation; 4350 reflections measured ($5.0\leq2\theta\leq50.0°$, $+h$, $+k$, $+l$,), 4350 unique giving 3096 with $I>3\sigma(I)$. Absorption correction by ψ scan method.

Structure Analysis and Refinement.[21] Structure was solved by direct methods (Rh and S atoms) followed by normal heavy-atom procedures. Full matrix least-squares refinement with all non-hydrogen atoms anisotropic and hydrogen at calculated positions. Hydrogen atoms except for the hydrido ligand were located at idealized positions and included in structure calculation without further refinement of the parameters. The position of hydrido ligand was located in D-map and refined with isotropic temperature factors. Final R and R_w values are obtained as 0.025 and 0.034, respectively, based on the calculation using weighting scheme $w=1/\sigma^2(F_o)$, with $\sigma(F_o)$ from counting statistics.

Atomic coordinates of the non-hydrogen atoms are listed in Table 2. The lists of structure factors, anisotropic thermal parameters of non-hydrogen atoms, and all bond distances and angles are deposited as Document No. 67072 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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10) Single crystal of **1** were obtained by recrystallization in acetone. Crystal data: $C_{18}H_{42}ClP_4RhS$, $M=552.87$, orthorhombic, $a=32.380(4)$, $b=11.469(2)$, $c=18.064(2)$ Å, $\beta=118.53(3)^\circ$, $U=5962$ Å^3 ($\lambda=0.71069$ Å), space group $C2$ (no.5), $Z=8$, $D_c=1.234$ g cm^{-3}, $F(000)=2192$. Crystal dimensions: 0.4×0.5×0.5 mm, $\mu(\text{Mo}\,K\alpha)=9.36$ cm^{-1}. Although data collection and structure determination revealed the structure, the calculation did not converge well, probably due to serious decay of the crystal during data collection [current R and $R_w=0.088$ and 0.092, respectively, for 3225 reflections with $I>3\sigma(I)$]. Details of the structure refinement will be reported elesewhere.

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