44 *Inorg. Chem.* **1984**, *23*, 44-48

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Reaction of H_2S with Phosphine Complexes of Rh(I) and Ir(I). Crystal and Molecular Structures of $[RhCl(H)(\mu\text{-}SH)(PPh_3)_2]_2\cdot 2CH_2Cl_2$ and $IrCl(H)(SH)CO(PPh_3)_2$

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Received April 14, 1983

The reaction of H_2S with $RhCl(PPh_3)_3$ and *trans*-$IrCl(CO)(PPh_3)_2$ in CH_2Cl_2 solutions leads to the formation of the SH^--bridged binuclear complex $[RhCl(H)(\mu\text{-}SH)(PPh_3)_2]_2\cdot 2CH_2Cl_2$ (**1**) and $IrCl(H)(SH)(CO)(PPh_3)_2$ (**2**), respectively. Both complexes are formed in high yield and are only slightly soluble in organic solvents. Crystals of both complexes have been obtained, and single-crystal X-ray diffraction analyses have been carried out. Complex **1** crystallizes in the monoclinic space group $P2_1/a$ with unit cell parameters $a = 23.830$ (5) Å, $b = 15.531$ (3) Å, $c = 9.788$ (3) Å, $\beta = 99.88$ (2)°, $V = 3569$ Å^3, $Z = 2$, and $d_{calcd} = 1.455$ g cm^{-3}, and the structure converged to a conventional R factor of 0.039 for 5125 observations and 406 parameters. Complex **2** crystallizes in the monoclinic space group $C2/c$ with unit cell parameters $a = 23.664$ (3) Å, $b = 9.685$ (2) Å, $c = 15.782$ (3) Å, $\beta = 115.33$ (2)°, $V = 3269$ Å^3, $Z = 4$, and $d_{calcd} = 1.654$ g cm^{-3}, and the structure converged to a conventional R factor of 0.022 for 4077 observations and 202 parameters. Complex **1** is a symmetrically SH^--bridged binuclear complex with a planar $Rh_2(\mu\text{-}S)_2$ grouping. The coordination geometry about each Rh is approximately octahedral with cis PPh_3 ligands and a trans Cl-Rh-H arrangement. The hydride and SH hydrogen atoms were refined, and the Rh-H distance is 1.59 (6) Å and the Cl-Rh-H angle is 170 (2)°. There is no Rh-Rh bonding interaction. Complex **2** has pseudooctahedral coordination geometry with trans PPh_3 ligands and trans H-Ir-Cl and HS-Ir-CO arrangements. The hydride ligand was refined to give an Ir-H distance of 1.47 (8) Å, and the H-Ir-Cl angle is 180° as required by a crystallographic C_2 axis, which is coaxial with this grouping. Both complexes have long M-Cl distances (2.519 (1) and 2.492 (3) Å for Rh and Ir, respectively), which result from the trans influence of the hydrido ligand. The stereochemistries of these complexes show that the oxidative addition of H_2S occurs cis in both cases.

Introduction

There has been considerable recent interest in complexes that contain H_2S[1,2] and SH^- ligands.[3,4] Some of this interest stems from the potential use of these complexes as models for biological systems;[5] however, more recently, the chemistry of SH^--containing complexes has been actively pursued because of its relevance to metal sulfide hydrodesulfurization catalysts.[6,7]

Our interest in this area stems from the potential use of H_2S as a source of H_2 and organosulfur compounds. We have embarked on a research program designed to find transition-metal catalysts for this purpose, and as part of this study we have examined the reaction chemistry between H_2S and various metal complexes. Very little has been reported in this area. We report here the isolation and X-ray structural characterization of the major products of the reactions between H_2S and $RhCl(PPh_3)_3$ and $IrCl(CO)(PPh_3)_2$, respectively. Although both of these reactions have been briefly mentioned in the literature,[8-10] the products have not been unambiguously characterized and for one product the incorrect formulation was proposed. The characterization reported here of $IrCl(H)(SH)CO(PPh_3)_2$ (**2**) is the first X-ray structural determination of an SH complex of iridium, and only one other SH complex of rhodium has been structurally characterized.[11]

Experimental Section

Reagents and Solvents. Iridium trichloride hydrate and rhodium trichloride hydrate were obtained from Johnson-Matthey, Inc. Reagent grade methylene chloride was passed down an activated basic alumina column prior to use. All of the remaining solvents were reagent grade and used without further purification.

Physical Measurements. Infrared spectra were recorded on a Beckman Model 4250 grating spectrophotometer using KBr pellets. ^1H NMR spectra were recorded at 300 MHz with a Nicolet NT-300 spectrometer. Chemical shifts are reported as δ values with positive shifts downfield. ^{31}P NMR spectra were obtained at 121 MHz. The chemical shifts are reported in ppm relative to the external standard 85% H_3PO_4 ($\delta = 0$) with positive shifts downfield. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Synthesis of the Compounds. All manipulations were carried out under a purified nitrogen atmosphere with use of standard Schlenk line techniques.

$IrCl(CO)(PPh_3)_2$ was prepared according to the published synthesis (method B) by Collman and Kang.[12]

$[RhCl(H)(SH)(PPh_3)_2]_2\cdot 2CH_2Cl_2$ (1) was prepared by stirring a solution of $RhCl(PPh_3)_3$ in degassed CH_2Cl_2 under an H_2S atmosphere. The solution immediately changed from deep red to pale orange. ^1H and ^{31}P NMR spectra were recorded of the reaction mixture immediately because the yellow precipitate that forms is only slightly soluble. Crystals were obtained by slow solvent diffusion with CH_2Cl_2 and diethyl ether. Compound **1** was isolated in 75% yield. IR (KBr disk): ν(Rh-H) = 2160 (m) cm^{-1}. $^{31}P\{^1H\}$ NMR (25 °C, CH_2Cl_2): δ 38.01 (doublet, $J_{Rh-P} = 116$ Hz), δ -4.88 (singlet, uncoordinated PPh_3). ^1H NMR in the hydride region (25 °C, CD_2Cl_2): δ -18.4 (multiplet). Anal. Calcd for $C_{72}H_{64}Cl_2P_4S_2Rh_2\cdot 2CH_2Cl_2$: C, 56.83; H, 4.38; P, 7.92; S, 4.07. Found: C, 56.42; H, 4.41; P, 7.98; S, 4.10.

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$IrCl(H)(SH)(CO)(PPh_3)_2$ (2) was prepared by stirring a solution of $IrCl(CO)(PPh_3)_2$ in either $CHCl_3$ or CH_2Cl_2 under an H_2S atmosphere. The solution changed from yellow to very pale yellow, and precipitation began immediately. Crystals were obtained by slow solvent diffusion of dilute solutions upon layering with diethyl ether. Compound **2** was isolated in 80% yield. IR (KBr disk): ν(Ir–H) = 2240 cm^{-1}; ν(CO) = 2015 cm^{-1}. $^{31}P\{^1H\}$ NMR at 25 °C (reaction mixture) recorded immediately during the reaction showed the presence of some uncoordinated PPh_3 (δ −4.9), but other resonances were not reproducible from experiment to experiment. The product is too insoluble for reliable NMR data. Anal. Calcd for $C_{37}H_{32}ClOP_2SIr$: C, 54.57; H, 3.96; Cl, 4.35; S, 3.94. Found: C, 53.2; H, 4.2; Cl, 3.6; S, 3.4.

Collection and Reduction of X-ray Data. A summary of crystal and intensity data for compounds **1** and **2** is presented in Table I. Crystals of both compounds were secured to the end of glass fibers with 5-min epoxy resin. The crystal class of each compound was determined by use of the Enraf-Nonius CAD 4-SDP peak search, centering, and indexing programs.[13] Background counts were measured at both ends of the scan range with the use of an ω–2θ scan, equal, at each side, to one-fourth of the scan range of the peak. In this manner, the total duration of background measurement is equal to half of the time required for the peak scan. The intensities of three standard reflections were measured every 1.5 h of X-ray exposure, and no decay with time was noted for either compound. The data were corrected for Lorentz, polarization, and background effects. An empirical absorption correlation was applied for compound **2** by use of ψ-scan data and programs PSI and EAC.[13]

Solution and Refinement of the Structures. Both structures were solved by conventional heavy-atom techniques. The metal atoms were located by Patterson syntheses. Full-matrix least-squares refinement and difference-Fourier calculations were used to locate all remaining non-hydrogen atoms as well as the metal hydride hydrogen atoms for both compounds and the SH hydrogen atom in **1**. The atomic scattering factors were taken from the usual tabulation,[14] and the effects of anomalous dispersion were included in F_c by using Cromer and Ibers'[15] values of $\Delta f'$ and $\Delta f''$. Tables of observed and calculated structure factor amplitudes are available.[16] Hydrogen atom positions were calculated (C–H distance set at 0.95 Å) for all phenyl ring hydrogen atoms in **1** and **2** and were included in structure factor calculations but were not refined. The metal hydrido (**1** and **2**) and hydrogen sulfido (**1** only) hydrogen atom positional and isotropic thermal parameters were included in the final full-matrix least-squares refinement. The SH hydrogen atom in **2** could not be located due to disorder between the mutually trans CO and SH ligands. Such a disorder is common in complexes of this type.[11] These two ligands are disordered about a crystallographic C_2 axis, which contains the Ir, H, and Cl atoms. A model that treated the S atom as thermally anisotropic and the C and O atoms as isotropic was used, and reasonable distances and angles were obtained (vide infra). An additional complication is that the assignment of sulfur and chlorine as shown in Figure 2 could not be verified by the X-ray determination. Refinements with the S and Cl labels interchanged lead to equally good solutions. This is in part due to the disorder between CO and its trans ligand. The assignment finally used (Figure 2) was based on spectroscopic data, which conclusively showed this to be the correct stereochemistry (vide infra).

For complex **2** a trial structure was found in the centric space group $C2/c$, which requires the PPh_3 ligands to be crystallographically equivalent but which also requires the SH and CO ligands to be disordered. Refinement in this space group converted to R = 0.022 with no indication of any unusual thermal motion within the PPh_3 ligands. The alternative refinement in the acentric space group Cc which would be required to remove the disorder would not require crystallographically equivalent PPh_3 ligands. The experimental result that they are equivalent is compelling evidence that $C2/c$ with disorder is the correct assignment.

Table I. Summary of Crystal Data and Intensity Collection for Compounds 1 and 2

	1	2
	Crystal Parameters	
cryst syst	monoclinic	monoclinic
space group	$P2_1/a$	$C2/c$
cell parameters		
a, Å	23.830 (5)	23.664 (3)
b, Å	15.531 (3)	9.685 (2)
c, Å	9.788 (3)	15.782 (3)
β, deg	99.88 (2)	115.33 (2)
V, $Å^3$	3569 (3)	3269 (2)
Z	2	4
calcd density, g cm^{-3}	1.455	1.654
abs coeff, cm^{-1}	7.1	45.9
max, min, av transmission factors		1.00, 0.85, 0.93
formula	$C_{72}H_{64}Cl_2P_2S_2Rh_2 \cdot CH_2Cl_2$	$C_{37}H_{32}ClOP_2SIr$
fw	1563.18	814.33
	Measurement of Intensity Data	
diffractometer	CAD 4	CAD 4
radiation	Mo K$\bar{\alpha}$ (λ = 0.710 69 Å)	Mo K$\bar{\alpha}$ (λ = 0.710 69 Å)
scan type	ω–2θ	ω–2θ
$2\theta_{max}$, deg	52	60
unique reflcns measd (region)	6984 ($\pm h, +k, +l$)	4764 ($\pm h, +k, +l$)
obsd reflcns[a]	5125 ($F_o^2 \geqslant 1.0\sigma(F_o^2)$)	4077 ($F_o^2 \geqslant 1.0\sigma(F_o^2)$)
refinement by full-matrix least-squares		
no. of parameters	406	202
R[b]	0.039	0.022
R_w[b]	0.052	0.026
GOF[b]	1.51	1.07
p[a]	0.04	0.03

[a] The intensity data were processed as described in: "CAD4 and SDP User's Manual"; Enraf-Nonius: Delft, Holland, 1978. The net intensity $I = [K/(NPI)](C - 2B)$, where K = 20.1166 × (attenuator factor), NPI = ratio of fastest possible scan rate to scan rate for the measurement, C = total count, and B = total background count. The standard deviation in the net intensity is given by $[\sigma(I)]^2 = (K/(NPI))^2[C + 4B + (pI)^2]$, where p is a factor used to downweight intense reflections. The observed structure factor amplitude F_o is given by $F_o = (I/Lp)^{1/2}$, where Lp = Lorentz and polarization factors. The $\sigma(I)$'s were converted to the estimated errors in the relative structure factors $\sigma(F_o)$ by $\sigma(F_o) = {}^1/_2[\sigma(I)/I]F_o$. [b] The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma(F_o)]^2$. The unweighted and weighted residuals are defined as $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$ and $R_w = [(\Sigma w(|F_o| - |F_c|))^2/(\Sigma w|F_o|)^2]^{1/2}$. The error in an observation of unit weight (GOF) is $[\Sigma w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, where NO and NV are the number of observations and variables, respectively.

The final difference Fourier maps for both compounds did not reveal chemically significant residual electron density. The final positional and thermal parameters of the refined atoms appear in Tables II and III and as supplementary material.[16] The labeling schemes for both compounds are presented in Figures 1 and 2.

Results and Discussion

Rhodium Chemistry. The reaction of H_2S with $RhCl(PPh_3)_3$ in CH_2Cl_2 solution leads to the immediate formation in good yield of the SH-bridged binuclear complex $[RhCl(H)(SH)(PPh_3)_2]_2 \cdot 2CH_2Cl_2$ (**1**) (vide infra). Complex **1** is only slightly soluble in CH_2Cl_2, and the yellow crystalline solid precipitates out of solution rapidly. It is possible to obtain a ^{31}P NMR spectrum of the reaction mixture prior to precipitation, how-

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(16) See paragraph at end of paper regarding supplementary material.

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for Compound **1**[a]

atom	x	y	z	B(iso eq), Å^2 [b]
Rh	0.02752 (1)	0.10818 (2)	0.53775 (3)	2.218
Cl	0.09869 (5)	0.04171 (7)	0.7286 (1)	3.68
Cl2	−0.19389 (13)	0.41960 (21)	0.9167 (3)	13.1
Cl3	−0.23924 (12)	0.54576 (19)	0.7152 (5)	17.4
S	0.04528 (4)	−0.01549 (7)	0.4076 (1)	3.74
P1	0.09591 (4)	0.18787 (6)	0.4512 (1)	2.48
P2	−0.01678 (4)	0.21862 (6)	0.6419 (1)	2.42
C1A	0.1573 (2)	0.2283 (3)	0.5732 (4)	2.8
C2A	0.1536 (2)	0.2378 (3)	0.7111 (5)	3.4
C3A	0.1992 (2)	0.2724 (4)	0.8031 (5)	4.6
C4A	0.2482 (2)	0.2966 (4)	0.7561 (6)	4.9
C5A	0.2524 (2)	0.2849 (3)	0.6202 (6)	4.9
C6A	0.2078 (2)	0.2507 (3)	0.5281 (5)	3.8
C1B	0.1317 (2)	0.1261 (3)	0.3324 (4)	3.0
C2B	0.1697 (2)	0.0627 (3)	0.3876 (5)	3.9
C3B	0.1979 (2)	0.0135 (3)	0.3030 (6)	5.6
C4B	0.1879 (3)	0.0260 (4)	0.1645 (6)	6.8
C5B	0.1488 (3)	0.0879 (5)	0.1065 (6)	7.0
C6B	0.1219 (2)	0.1382 (4)	0.1906 (5)	4.7
C1C	0.0701 (2)	0.2826 (3)	0.3473 (4)	2.9
C2C	0.0160 (2)	0.2807 (3)	0.2665 (5)	3.7
C3C	−0.0051 (2)	0.3507 (4)	0.1862 (5)	4.8
C4C	0.0278 (2)	0.4236 (3)	0.1863 (5)	5.4
C5C	0.0813 (2)	0.4267 (3)	0.2631 (5)	4.7
C6C	0.1024 (2)	0.3564 (3)	0.3429 (5)	3.9
C1D	0.0227 (2)	0.3175 (3)	0.7023 (4)	3.0
C2D	0.0316 (2)	0.3804 (3)	0.6066 (5)	3.6
C3D	0.0666 (2)	0.4503 (3)	0.6476 (6)	4.7
C4D	0.0934 (2)	0.4573 (3)	0.7818 (6)	5.3
C5D	0.0841 (2)	0.3972 (3)	0.8777 (5)	4.6
C6D	0.0485 (2)	0.3277 (3)	0.8381 (5)	3.7
C1E	−0.0431 (2)	0.1857 (3)	0.8003 (4)	2.8
C2E	−0.0111 (2)	0.1292 (3)	0.8904 (4)	3.6
C3E	−0.0288 (2)	0.1060 (3)	1.0133 (5)	4.4
C4E	−0.0778 (2)	0.1393 (3)	1.0473 (4)	4.4
C5E	−0.1088 (2)	0.1974 (4)	0.9601 (5)	4.8
C6E	−0.0926 (2)	0.2201 (3)	0.8352 (4)	3.9
C1F	−0.0813 (2)	0.2605 (3)	0.5289 (4)	3.0
C2F	−0.1104 (2)	0.2110 (3)	0.4224 (4)	3.5
C3F	−0.1585 (2)	0.2425 (4)	0.3368 (5)	4.9
C4F	−0.1778 (2)	0.3251 (4)	0.3588 (6)	5.4
C5F	−0.1499 (2)	0.3734 (3)	0.4657 (6)	4.9
C6F	−0.1019 (2)	0.3424 (3)	0.5500 (5)	3.8
C	−0.2468 (3)	0.4449 (5)	0.7820 (10)	9.4
H	−0.012 (2)	0.141 (3)	0.400 (5)	5 (1)
H1	0.028 (3)	0.000 (5)	0.306 (7)	7 (2)

[a] Anisotropic thermal parameters and calculated hydrogen atom positional parameters are included as supplementary material. [b] $B(\text{iso eq}) = {}^1/_3(B_{11} + B_{22} + B_{33})$.

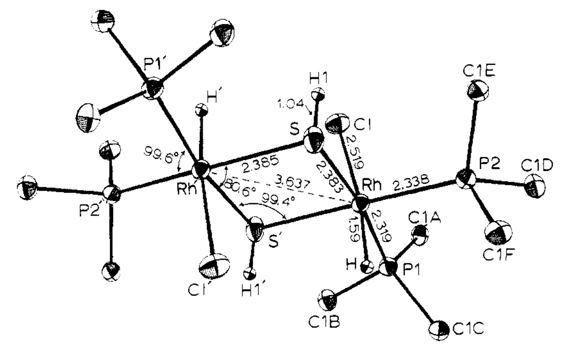

Figure 1. ORTEP drawing of $[RhCl(H)(SH)(PPh_3)_2]_2$ (**1**) showing the molecular structure and labeling scheme. Phenyl carbon atoms have been omitted for clarity and are labeled C1A, C2A, ..., C6A for ring A, etc. The primed atoms are related to their unprimed counterparts by a crystallographic inversion center, which is located at the midpoint of the Rh- - -Rh′ vector.

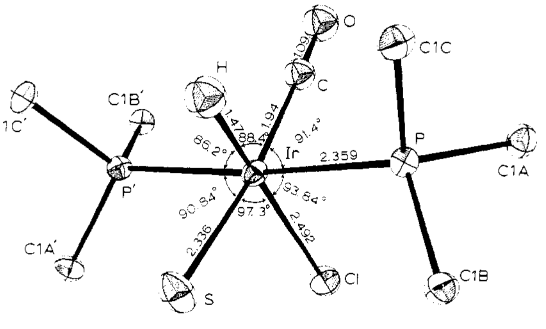

Figure 2. ORTEP drawing of $IrCl(H)(SH)(CO)(PPh_3)_2$ (**2**) showing the molecular structure and labeling scheme. Phenyl carbon atoms have been omitted for clarity and are labeled C1A, C2A, ..., C6A for ring A, etc. The primed atoms are related to their unprimed counterparts by a crystallographic C_2 axis, which passes through the Ir, H, and Cl atoms. The C_2 axis requires that CO and S are mutually disordered; however, an ordered version is shown in the figure (see text).

Table III. Positional and Thermal Parameters for Compound **2**[a]

atom	x	y	z	B(iso eq), Å^2 [c]
Ir	0.0000 (0)	0.19058 (1)	0.2500 (0)	1.865
Cl	0.0000 (0)	0.44790 (9)	0.2500 (0)	2.93
S[b]	0.05220 (7)	0.1598 (2)	0.41211 (9)	3.20
P	−0.09516 (3)	0.17424 (6)	0.26388 (4)	1.89
O[b]	−0.0670 (2)	0.1794 (5)	0.0382 (3)	4.13 (9)
C1A	−0.1621 (1)	0.2731 (3)	0.1832 (2)	2.44
C2A	−0.1581 (1)	0.3593 (3)	0.1155 (2)	2.56
C3A	−0.2101 (1)	0.4350 (3)	0.0565 (2)	3.10
C4A	−0.2651 (1)	0.4251 (4)	0.0644 (2)	4.0
C5A	−0.2696 (1)	0.3429 (4)	0.1321 (2)	5.2
C6A	−0.2183 (1)	0.2667 (4)	0.1920 (2)	4.28
C1B	−0.0910 (1)	0.2308 (3)	0.3766 (2)	2.23
C2B	−0.0993 (1)	0.1432 (3)	0.4398 (2)	3.35
C3B	−0.0953 (2)	0.1959 (4)	0.5247 (2)	4.37
C4B	−0.0837 (2)	0.3328 (4)	0.5457 (2)	4.09
C5B	−0.0749 (2)	0.4193 (4)	0.4839 (2)	5.6
C6B	−0.0781 (2)	0.3691 (3)	0.3999 (2)	4.87
C1C	−0.1201 (1)	−0.0059 (3)	0.2505 (2)	2.52
C2C	−0.1766 (1)	−0.0501 (3)	0.1812 (2)	3.26
C3C	−0.1909 (2)	−0.1907 (3)	0.1703 (2)	4.6
C4C	−0.1497 (2)	−0.2860 (3)	0.2285 (2)	5.3
C5C	−0.0938 (2)	−0.2438 (3)	0.2974 (3)	4.8
C6C	−0.0787 (1)	−0.1044 (3)	0.3087 (2)	3.29
C[b]	−0.0433 (2)	0.1850 (6)	0.1146 (4)	2.91 (9)
H	0.0000 (0)	0.039 (5)	0.2500 (0)	4 (1)

[a] Anisotropic thermal parameters and calculated hydrogen atom positional parameters are included as supplementary material. [b] Atoms disordered on opposite sides of Ir due to C_2 symmetry axis (see text). [c] $B(\text{iso eq}) = {}^1/_3(B_{11} + B_{22} + B_{33})$.

ever, and resonance due to **1** (δ 38.01, doublet, J_{Rh-P} = 116 Hz) and uncoordinated PPh_3 (δ −4.88) are present. A metal hydride resonance is also apparent in the ^1H NMR spectrum of the reaction mixture (δ −18.4, multiplet), and a Rh–H stretching variation is observed in the IR spectrum: ν = 2160 cm^{-1}. This reaction has previously been reported by Singer and Wilkinson,[8] and they apparently isolated the same insoluble product. However, they formulated the complex to the unusual CH_2Cl_2-solvated mononuclear species $RhCl(H)(SH)(PPh_3)_2 \cdot 0.5CH_2Cl_2$ and based this formulation on elemental analysis data. We see no evidence for this mononuclear complex, and we have carried out the syntheses many

Table IV. Selected Distances and Angles in **1**[a]

			Distances, Å				
Rh-Rh′	3.637 (1)	Rh-S	2.383 (1)	P1-C1B	1.827 (4)	P2-C1F	1.851 (4)
Rh-P1	2.319 (1)	Rh-S′	2.385 (1)	P1-C1C	1.833 (4)	C-Cl2	1.71 (1)
Rh-P2	2.338 (1)	Rh-H	1.59 (6)	P2-C1D	1.845 (4)	C-Cl3	1.72 (1)
Rh-Cl	2.519 (1)	P1-C1A	1.833 (4)	P2-C1E	1.842 (4)		
			Angles, deg				
P1-Rh-S′	171.09 (4)	P1-Rh-H	82 (2)	Cl-Rh-S	84.69 (5)	Rh-S-H1	104 (2)
P2-Rh-S	163.66 (4)	P1-Rh-S	91.97 (4)	Cl-Rh-S′	90.53 (5)	Rh-S′-H1′	99 (2)
Cl-Rh-H	170 (2)	P2-Rh-Cl	105.93 (4)	H-Rh-S	87 (2)	Rh-S-Rh′	99.43 (4)
P1-Rh-P2	99.55 (4)	P2-Rh-H	83 (2)	H-Rh-S′	92 (2)	Cl2-C-Cl3	113.1 (5)
P1-Rh-Cl	93.65 (4)	P2-Rh-S′	86.84 (4)	S-Rh-S′	80.57 (4)		

[a] The primed atoms are related to their unprimed counterparts by an inversion center of symmetry.

times using a procedure identical with that of Wilkinson.[8] We conclude that only the binuclear complex **1** is formed as a solid product of this reaction, and satisfactory analytical data have been obtained for this formulation. In order to verify the correct formulation and structure of **1**, a single-crystal X-ray diffraction study was carried out. Additionally, the X-ray structure determination was easily justified because of the recent interest in SH complexes in general[1-7] and because only one other SH complex of rhodium has been characterized by single-crystal X-ray analysis.[11]

The crystal structure of **1** consists of well-separated $[RhCl(H)(SH)(PPh_3)_2]_2$ dimers and CH_2Cl_2 solvate molecules. The shortest contact between the CH_2Cl_2 solvate and the binuclear complex is 3.14 Å for $Cl3 \cdots H_2B$. The structure of the binuclear complex is shown in Figure 1, and selected distances and angles are listed in Table IV. The molecule contains an inversion center of symmetry at the midpoint of the Rh–Rh′ vector, and therefore the RhRh′SS′ four-membered ring is exactly planar. The SH groups symmetrically bridge the two Rh atoms, and H1 and H1′ are positioned trans to each other as required by the inversion center of symmetry. The intramolecular Rh···Rh′ (3.637 (1) Å) and the S···S′ (3.083 (2) Å) separations are consistent with nonbonding interactions.[17] The coordination around each Rh atom is almost octahedral with the most significant distortion being caused by steric repulsion between the bulky PPh_3 groups and the chloride ligand. Thus, the P1–Rh–P2 and S–Rh–S′ angles are 99.55 (4) and 80.57 (4)°, respectively, and P2–Rh–Cl is 105.93 (4)°.

The two Rh–S distances of 2.385 (1) and 2.383 (1) Å compare well with the Rh–S distances in μ-SR bridged complexes (2.38 Å in $Rh_2(\mu\text{-}SPh)_2(CO)_2(PMe_3)_2$[17] and 2.39 Å in $(\pi\text{-}C_5H_5)_2Mo(\mu\text{-}SMe)_2Rh(C_3H_5)_2$[18]). The Rh–P distances of 2.338 (1) and 2.319 (1) Å are somewhat shorter than is usually observed for Rh(III) complexes when phosphine ligands are mutually trans (2.36–2.41 Å)[19] but compare well with those where the phosphines are cis.[20] The Rh–Cl distance of 2.519 (1) Å is long, due to the trans influence of the hydride ligand.[19] The hydride and hydrogen sulfido hydrogen atoms were both located and defined by full-matrix least squares in the X-ray analysis. The Rh–H distance of 1.59 (6) Å falls within the range of 1.5–1.7 Å normally observed for second-row transition-metal hydrides,[19,21] and the Cl–Rh–H angle of 170 (2)° is close to the 180° value expected for trans stereochemistry. The angles around the bridging S atom are in agreement with approximate sp^3 hybridization (Rh–S–H1 = 104 (2)°, Rh–S′–H1′ = 99 (2)°, and Rh–S–Rh′ = 99.43 (4)°) as expected in μ-SH complexes. The Rh–H and S–H vectors are almost parallel with cis and trans orientations about the Rh–S bonds. Thus the dihedral angles for H–Rh–S–H1 and H–Rh–S′–H′ are 168 and 9°, respectively. The entire $P_2RhS_2RhP_2$ coordination core is approximately planar. The deviations of Rh and S from the plane formed by the four phosphorus atoms are 0.17 and 0.10 Å, respectively.

Table V. Selected Distances and Angles in **2**[a]

	Distances, Å		
Ir-P	2.359 (2)	C-O	1.09 (4)
Ir-Cl	2.492 (3)	P-C1A	1.823 (4)
Ir-S	2.336 (4)	P-C1B	1.823 (4)
Ir-C	1.94 (2)	P-C1C	1.825 (5)
Ir-H	1.47 (8)		
	Angles, deg		
P-Ir-C	91.4 (4)	S-Ir-H	83 (1)
P-Ir-S	88.18 (8)	S-Ir-P′	90.84 (6)
P-Ir-Cl	93.84 (5)	C-Ir-P′	88.4 (3)
P-Ir-H	86 (1)	C-Ir-H	88 (2)
P-Ir-P′	172.31 (5)	Ir-C-O	178 (1)
Cl-Ir-C	91.6 (5)	Ir-P-C1A	118.6 (2)
Cl-Ir-S	97.3 (1)	Ir-P-C1B	114.5 (2)
Cl-Ir-H	180[b]	Ir-P-C1C	109.1 (2)
S-Ir-C	171.1 (5)		

[a] The primed atoms are related to their unprimed counterparts by a twofold axis. [b] Required by crystallographic symmetry.

Iridium Chemistry. The oxidative addition of H_2S to *trans*-$IrCl(CO)(PPh_3)_2$ has been briefly mentioned in the literature.[8-10] The stereochemistry of the addition product $IrCl(H)(SH)(CO)(PPh_3)_2$ (**2**) has been proposed to be consistent with a cis addition; i.e., H and SH are cis, the PPh_3 ligands are mutually trans, and H is trans to Cl. This assignment was based entirely on the position of IR stretching frequencies (ν(Ir–Cl) $\simeq$ 265 cm^{-1} and ν(Ir–H) is greater than 2200 cm^{-1}), which suggests that H is trans to Cl.[8] Additional support for this assignment is provided by the study of the oxidative addition of para-substituted benzenethiols to *trans*-$IrX(CO)(PPh_3)_2$ (X = Cl, Br, I).[22] IR and ^1H NMR data for the product $IrX(H)(SC_6H_4Y)(CO)(PPh_3)_2$ show that ν(CO) is a linear function of the Hammett substituent parameter, σ_p, and δ(Ir–H), for a given ligand X, is invariant to the nature of the para substituent Y. It was also noted that ν(Ir–H) decreased with increasing trans influence of the halogen X and that the changes in δ(Ir–H) as X is varied follow the general trend noted in the literature for trans H–M–X stereochemistry.[23]

Complex **2** is insoluble in all organic solvents, and therefore NMR spectra of the complex could not be obtained. However, ^{31}P NMR spectra of the reaction mixture of H_2S and *trans*-$IrCl(CO)(PPh_3)_2$ showed the presence of some uncoordinated PPh_3. At this point solid complex **2** had precipiated out. The presence of free PPh_3 suggests that the Ir analogue of **1** may

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also be formed in low yield; however, the 80% yield of **2** shows it to be the major product. A single-crystal X-ray diffraction analysis of **2** was carried out because of out interest in dihydrogen sulfide addition products and because there have been no previous structure determinations on hydrogen sulfido complexes of iridium.

The crystal structure of **2** consists of well-separated $IrCl(H)(SH)CO(PPh_3)_2$ molecules. The molecular structure of **2** is shown in Figure 2, and selected distances and angles are listed in Table V. The molecule possesses a crystallographic C_2 axis, which passes through the Ir, Cl, and H atoms. This symmetry requires that the CO and SH groups are disordered; however, a satisfactory model was found (see Experimental Section). Although the assignment of S and Cl as shown in Figure 2 could not be determined unambiguously from the X-ray analysis (see Experimental Section), the stereochemistry of the complex was chosen from the spectroscopic arguments presented above. The refinement converged with $R = 0.022$ with this model; however, an equally good solution was found ($R = 0.023$) with a model in which the S and Cl labels were interchanged. We consider the correct stereochemistry to be that shown in Figure 2. The hydrido ligand was located by difference-Fourier synthesis, and its positional and thermal parameters were refined. The hydrogen sulfido hydrogen atom could not be located due to the disorder in this ligand.

The coordination geometry in **2** is essentially octahedral as expected for an Ir(III) complex. The primary distortion from ideal octahedral geometry is a slight bending of the P, CO, and SH ligands toward the sterically less demanding hydride ligand. The hydride hydrogen was refined to a chemically reasonable position. The H–Ir–Cl angle is required to be 180° by the C_2 symmetry and is consistent with the spectroscopic prediction of trans H and Cl ligands. The Ir–H distance, 1.47 (8) Å, is somewhat shorter than that observed in other Ir(III) hydride complexes[24,25] and transition-metal hydrides in general (~1.7 Å).[26] This distance is similar to the value of 1.5 (1) Å found in $IrCl(H)[\eta^3\text{-}C_3H_4(1\text{-}Ph)](PPh_3)_2$,[27] which also has trans H–Ir–Cl stereochemistry and reflects the weak trans influence of the chloro ligand as does the high value of ν(Ir–H).[28]

The Ir–Cl bond length is at the high end of the range normally found, 2.492 (3) Å, presumably as a result of the trans influence of the strongly bound hydrido ligand. Iridium(III)–chlorine bond distances from 2.33 to 2.51 Å are generally found, and a distance of 2.549 (2) Å has been reported for a similar trans H–Ir–Cl complex.[27]

The angles in the trans SH–Ir–CO grouping are reasonable (S–Ir–C = 171.1 (5)° and Ir–C–O = 178 (1)°) as are the distances, which show that the model used for these disordered ligands is satisfactory. The Ir–S distance of 2.336 (4) Å is similar to values found in alkylthiolato complexes of Ir(III).[29] The distances and angles within the trans PPh_3 ligands (P–Ir–P′ = 172.31 (5)°) are normal.

Acknowledgment. Support for this research through a grant from the National Science Foundation (Grant CHE 81-08490) is gratefully acknowledged. We thank the Johnson-Matthey Co. for a generous loan of the precious metal salts. P.B. is the recipient of a Lando Summer Research Fellowship for 1982.

Registry No. **1**, 87901-22-2; **2**, 21157-61-9; $RhCl(PPh_3)_3$, 14694-95-2; *trans*-$IrCl(CO)(PPh_3)_2$, 15318-31-7.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom positional parameters, least-squares planes, and structure factor amplitudes for both compounds (50 pages). Ordering information is given on any current masthead page.

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