Inorg. Chem. **1982**, *21*, 2857–2859

Contribution from the Department of Chemistry,
Northwestern University, Evanston, Illinois 60201

Formal Insertion of Sulfur into a Metal–Hydride Bond: Formation of $Rh(SH)(CO)(P(C_6H_5)_3)_2$ from $RhH(P(C_6H_5)_3)_4$ and COS

THOMAS R. GAFFNEY and JAMES A. IBERS*

Received November 6, 1981

The reaction of $RhH(PPh_3)_4$ with carbonyl sulfide affords *trans*-mercaptocarbonylbis(triphenylphosphine)rhodium(I), $Rh(SH)(CO)(PPh_3)_2$, in high yield. The product has been characterized by infrared, ^1H, and $^{31}P\{^1H\}$ NMR spectroscopy and by an X-ray structure determination. A pathway to the formation of the compound is proposed that involves η^2 coordination of the COS molecule to the metal center, with subsequent hydride transfer to the sulfur atom and C–S bond cleavage.

Introduction

There are many examples of reactions that involve formal insertion of CO_2,[1] COS,[2-5] and CS_2[6] into metal–ligand bonds. Carbon dioxide and carbon disulfide formal insertions into metal–hydride bonds to form formates and dithioformates are well-known and have recently received attention because of their possible relevance to the catalysis of the water gas shift reaction.[7] There appears to be but one example of COS insertion into a metal–hydride bond[8] to form a monothioformate. We recently reported[9] that COS, unlike CS_2,[10] does not insert into the metal–hydride bond of $RuClH(CO)(PCy_3)_2$ (Cy = cyclohexyl) but rather carbonylates the compound to afford $RuClH(CO)_2(PCy_3)_2$. Here we report that the reaction of $RhH(PPh_3)_4$ with COS also results in carbonylation, but concomitantly the sulfur atom formally inserts into the metal–hydride bond to yield the mercapto complex *trans*-$Rh(SH)(CO)(PPh_3)_2$.

Experimental Section

Reactions were performed under an atmosphere of N_2 in solvents that were freshly distilled from sodium under N_2. Carbonyl sulfide was obtained from the Matheson Gas Co., East Rutherford, NJ, and was purified of H_2S and H_2O contaminants by reaction with lead acetate and subsequent distillation from calcium sulfate. The compound $RhH(PPh_3)_4$ was prepared as previously described.[11] Nuclear magnetic resonance spectra were recorded on a JEOL Fx90Q spectrometer at 89.59 (^1H) and 36.2 (^{31}P) MHz. Peak positions are relative to tetramethylsilane and 85% phosphoric acid, with downfield values reported as positive. Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer. Elemental analyses were performed by Micro-Tech Laboratories, Inc., Skokie, IL.

***trans*-Mercaptocarbonylbis(triphenylphosphine)rhodium(I), $Rh(SH)(CO)(PPh_3)_2$.** Upon addition of 3.0 mL of COS (0.12 mmol) to a suspension of $RhH(PPh_3)_4$ (0.108 g, 0.094 mmol) in 2.0 mL of toluene, the color of the suspension turned from yellow to orange. The suspension was stirred for 10 min and then combined with 10 mL of hexane. The yellow solid was collected by filtration, washed with hexane, and dried under vacuum. The yield was 0.043 g (67%). Anal. Calcd for $C_{37}H_{31}OP_2RhS$: C, 64.54; H, 4.54; S, 4.66. Found: C, 64.42; H, 4.69; S, 4.61. ^1H NMR: δ 7.57, 7.40 (C_6H_5, m), −1.21 (SH, dt, $^2J(^{103}Rh–^1H) = 1.6$ Hz, $^3J(^{31}P–^1H) = 18.1$ Hz). ^{31}P NMR: δ 36.2 (d, $J(^{103}Rh–^{31}P) = 130.6$ Hz). The spectra were recorded in $CDCl_3$ at −40 °C. IR: $\nu(CO) = 1959\ cm^{-1}$ (vs, in Nujol).

Crystallographic Study of *trans*-$Rh(SH)(CO)(PPh_3)_2\cdot CHCl_3$. Yellow crystals suitable for X-ray diffraction studies were obtained as the $CHCl_3$ solvate from a chloroform/hexane solution of *trans*-$Rh(SH)(CO)(PPh_3)_2$ at −30 °C. The crystals were mounted in capillaries under a chloroform-saturated argon atmosphere to prevent loss of the $CHCl_3$ of crystallization. Preliminary photographic data showed the crystals to belong to the monoclinic system with systematic extinctions ($h0l$, $l \neq 2n$; hkl, $h + k \neq 2n$; $0k0$, $k \neq 2n$) consistent with the space groups C_s^4—Cc or C_{2h}^6—$C2/c$.

Data collection was carried out on a computer-controlled Picker four-circle diffractometer with the crystal in a stream of N_2 at −158 °C. Unit cell dimensions at −158 °C are $a = 12.382$ (4), $b = 14.196$ (5) Å, $c = 20.309$ (6) Å, $\beta = 93.92$ (1)°, $V = 3561$ Å^3, and $Z = 4$; ρ_{calcd} (−158 °C) = 1.506 g/cm^3 for $C_{38}H_{32}Cl_3OP_2RhS$ and ρ_{obsd} (25 °C) = 1.46 (3) g/cm^3. The intensities of 7913 reflections ($\pm h,-k,-l$; $h + k = 2n$) were measured out to $2\theta = 63.8$ with Mo $K\alpha$ radiation and methods standard in this laboratory.[12] The data were processed as previously described.[12] An absorption correction was applied to the data ($\mu = 8.73\ cm^{-1}$, crystal volume 0.40 mm^3, transmission factors 0.531–0.585). The 5686 unique reflections having $F_o^2 > 3\sigma(F_o^2)$ were used in subsequent calculations.

The space group C_{2h}^6–$C2/c$ was assumed. This assumption is justified by the excellent subsequent refinement of the structure and the location of hydrogen atoms on the phenyl rings in difference electron density maps. With 4 formula units in $C2/c$, the metal complex must have C_2 symmetry with trans phosphine ligands and disordering of the CO and SH ligands. The rhodium, sulfur, and phosphorus atoms were located from a sharpened, origin-removed Patterson synthesis. Subsequent structure factor calculations and Fourier syntheses revealed the positions of the remaining nonhydrogen atoms. Resolution of the disordered S and CO atoms was possible, probably because of the low-temperature data set. Symmetry C_2 is also imposed on the $CHCl_3$ solvate molecule. In this instance the symmetry axis is sufficiently close to atom Cl(2) so that this atom was refined with full occupancy. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and where $w = 4F_o^2/\sigma^2(F_o^2)$. The phenyl rings were treated as rigid groups[13] with C–C distances of 1.395 Å and ideal D_{6h} symmetry. Each group atom was refined with an individual isotropic thermal parameter. All other nonhydrogen atoms were refined anisotropically. Phenyl and chloroform hydrogen atoms were idealized with a C–H distance of 0.95 Å. These hydrogen atoms were included as fixed contributions in the final refinement that converged to values of R and R_w of 0.047 and 0.082, respectively. An analysis of $\sum w(|F_o|$

---

(1) Eisenberg, R.; Hendriksen, D. E. *Adv. Catal.* **1979**, *28*, 79–172 and references therein.

(2) Arduini, A. L.; Jamerson, J. D.; Takats, J. *Inorg. Chem.* **1981**, *20*, 2474–2479.

(3) Busetto, L.; Palazzi, A.; Foliadis, V. *Inorg. Chim. Acta* **1980**, *40*, 147–152.

(4) Chisholm, M. H.; Extine, M. W. *J. Am. Chem. Soc.* **1977**, *99*, 782–792.

(5) Chisholm, M. H.; Extine, M. W. *J. Am. Chem. Soc.* **1977**, *99*, 792–802.

(6) Yaneff, P. V. *Coord. Chem. Rev.* **1977**, *23*, 183–220 and references therein.

(7) Darensbourg, D. J.; Rokicki, A.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1981**, *103*, 3223–3224.

(8) Ashworth, T. V.; Nolte, M.; Singleton, E. *J. Organomet. Chem.* **1976**, *121*, C57–C60. One additional example has been reported since this paper was prepared. See: Darensbourg, D. J.; Rokicki, A. *J. Am. Chem. Soc.* **1982**, 104, 349–350.

(9) Gaffney, T. R.; Ibers, J. A. *Inorg. Chem.*, in press.

(10) Moers, F. G.; Ten Hoedt, R. W. M.; Langhout, J. P. *J. Organomet. Chem.* **1974**, *65*, 93–98.

(11) Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 58–59.

(12) See, for example: Waters, J. M.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3273–3277. The low-temperature system is based on a design by: Huffman, J. C. Ph.D. Thesis, Indiana University, 1974. The diffractometer was run under the Vanderbilt disk oriented system (Lenhert, P. G. *J. Appl. Crystallogr.* **1975**, *88*, 568–570).

(13) La Placa, S. J.; Ibers, J. A. *Acta Crystallogr.* **1965**, *18*, 511–519.

0020-1669/82/1321-2857$01.25/0

Table I. Positional Parameters for the Atoms of $Rh(SH)(CO)(PPh_3)_2 \cdot CHCl_3$

atom	x^a	y	z
Rh	0	0.246 923 (15)	1/4
Cl(1)	0.071 003 (71)	0.092 880 (68)	0.696 977 (42)
Cl(2)	0.018 70 (43)	0.267 81 (15)	0.762 59 (20)
P	0.092 901 (52)	0.252 047 (34)	0.352 737 (31)
S	0.169 62 (21)	0.251 23 (11)	0.197 713 (91)
C(1)	0.373 78 (65)	0.255 38 (39)	−0.214 38 (33)
O	0.290 01 (51)	0.253 77 (42)	−0.191 21 (34)
C(2)	−0.029 91 (44)	0.157 13 (48)	0.735 66 (29)
H	0.238 1	0.250 0	0.250 0
C(11)	0.148 15 (12)	0.369 357 (78)	0.372 851 (69)
C(12)	0.152 07 (12)	0.435 359 (99)	0.322 382 (54)
C(13)	0.197 06 (13)	0.523 811 (89)	0.335 490 (64)
C(14)	0.238 13 (13)	0.546 261 (83)	0.399 068 (74)
C(15)	0.234 22 (13)	0.480 26 (11)	0.449 538 (56)
C(16)	0.189 23 (13)	0.391 806 (94)	0.436 430 (60)
C(21)	0.020 23 (12)	0.224 91 (11)	0.426 494 (65)
C(22)	−0.057 50 (13)	0.288 853 (96)	0.444 810 (79)
C(23)	−0.114 50 (13)	0.271 63 (11)	0.500 323 (86)
C(24)	−0.093 77 (13)	0.190 47 (13)	0.537 521 (71)
C(25)	−0.016 04 (14)	0.126 526 (99)	0.519 205 (75)
C(26)	0.040 96 (12)	0.143 75 (10)	0.463 692 (78)
C(31)	0.206 90 (10)	0.169 320 (93)	0.359 601 (80)
C(32)	0.309 92 (12)	0.193 422 (86)	0.385 960 (84)
C(33)	0.392 586 (91)	0.126 79 (11)	0.388 618 (92)
C(34)	0.372 22 (11)	0.036 06 (10)	0.364 917 (96)
C(35)	0.269 20 (13)	0.011 963 (85)	0.338 558 (93)
C(36)	0.186 537 (95)	0.078 59 (10)	0.335 900 (85)

[a] Estimated standard deviations in the least significant figures are given in this and all subsequent tables.

$- |F_c|)^2$ as a function of $|F_o|$, setting angles, and Miller indices revealed no significant trends. The highest peaks in the final difference electron density map are located near phenyl carbon atoms and are approximately 10% of the height of a typical carbon atom in this structure. A peak was located at $x = 0.2381$, $y = 0.2500$, and $z = 0.2500$, 1.3 Å from the sulfur atom (∠Rh–S–peak = 100°) with a height of 0.47 e/Å. Although it is reasonable to attribute this peak to a mercaptide half-hydrogen atom, we did not attempt to refine its position.

The final values of the positional parameters are given in Table I. Thermal parameters are given in Table II[14] while Table III[14] gives the calculated positions of the phenyl and chloroform hydrogen atoms. A listing of the observed and calculated structure amplitudes is given in Table IV.[14]

Results and Discussion

The reaction of $RhH(PPh_3)_4$ with COS affords the mercapto compound *trans*-$Rh(SH)(CO)(PPh_3)_2$,[15] as deduced from infrared, ^1H, and $^{31}P\{^1H\}$ NMR spectroscopy and a crystal structure determination of the product.

A mercaptide proton resonance was observed in the ^1H NMR spectrum (Figure 1). The position and splitting of the resonance are consistent with the assignment as a SH proton, split into a triplet by two equivalent phosphorus nuclei, and further split into a doublet by coupling to ^{103}Rh. No S–H stretch was observed in the infrared spectrum of $Rh(SH)(CO)(PPh_3)_2$. Mercaptide stretches in metal–mercapto complexes are generally weak and often are not observed.[16,17]

The crystal structure consists of the packing of discrete monomeric units of $Rh(SH)(CO)(PPh_3)_2$ and chloroform solvent molecules. A stereoview of the contents of one unit cell is shown in Figure 2 and is drawn without displaying the disorder. There are no unusual intermolecular contacts. No hydrogen-bonding interactions are observed that involve the mercapto hydrogen atom.

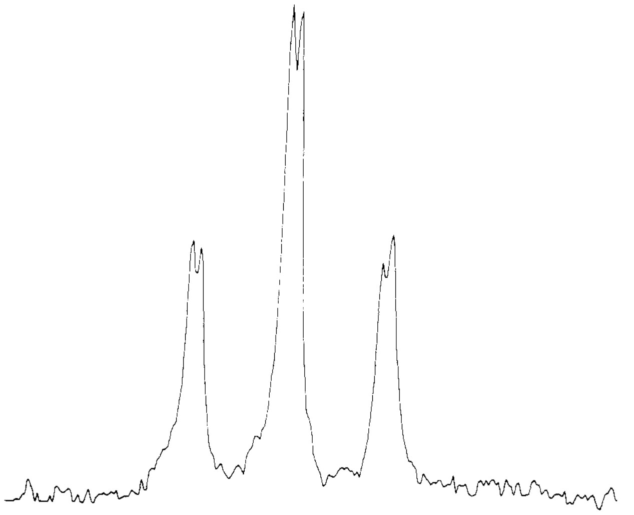


Figure 1. ^1H NMR spectrum of the mercaptide proton of $Rh(SH)(CO)(PPh_3)_2$ in $CDCl_3$ at −40 °C: δ −1.21, $^3J(^{31}P–^1H) = 18.1$ Hz, $^2J(^{103}Rh–^1H) = 1.6$ Hz.

The geometry about the central rhodium atom is approximately square planar. This near planarity is reflected by the distances of Rh, P, C(1), O, and S (Rh = 0.0195 (2) Å, S = 0.0019 (16) Å, P = −0.0533 (5) Å, C(1) = 0.020 (6), O = −0.023 (7) Å) from the best-weighted least-squares plane through the inner coordination sphere. The inner coordination sphere is shown in Figure 3. The mercapto hydrogen position shown is that located on the final difference electron density map but not refined. The Rh–P, Rh–C, and C–O distances are within the normal ranges (Table V). The Rh–S distance is longer than the distances reported for other group 8 mercapto complexes[18–21] (Table VI). This lengthening reflects the trans influence of the carbonyl group on the mercapto ligand.

A possible pathway of this reaction is shown in Scheme I. Replacement of one PPh_3 ligand by COS could lead to a η^2-COS-bound intermediate. Subsequent hydride transfer to sulfur and C–S bond cleavage could lead to the formation of $Rh(SH)(CO)(PPh_3)_2$. Carbon–sulfur bond cleavage in η^2-bound COS ligands is a facile process,[22–25] and formation of mercapto ligands from metal sulfides and hydrogen has recently been reported.[26] However, we have detected no intermediates nor have we made any kinetic measurements. Consequently, other conceivable pathways cannot be eliminated.

Examples of CO_2 and CS_2 insertions into metal–hydride bonds are numerous and invariably formation of formate and dithioformate ligands.[1,6,7] An example is known[9] of carbonylation of a metal–hydride complex through C═S cleavage of COS, but there is no precedence for insertion of a chalcogen atom of CO_2, COS, or CS_2 into a metal–hydride bond.[27] Our results suggest that reactions that result in C═S bond cleavage

---

(14) Supplementary material.

(15) This complex has been reported previously (Flynn, B. R.; Vaska, L. *J. Am. Chem. Soc.* **1973**, *95*, 5081–5083), but few details of the synthesis by another method and no details of the characterization were given.

(16) Collman, J. P.; Rothrock, R. K.; Stark, R. A. *Inorg. Chem.* **1977**, *16*, 437–440.

(17) Singer, H.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 2516–2520.

(18) Di Vaira, M.; Midollini, S.; Sacconi, L. *Inorg. Chem.* **1978**, *17*, 816–819.

(19) Di Vaira, M.; Midollini, S.; Sacconi, L. *Inorg. Chem.* **1977**, *16*, 1518–1524.

(20) Briant, C. E.; Hughes, G. R.; Minshall, P. C.; Mingos, D. M. P. *J. Organomet. Chem.* **1980**, *202*, C18–20.

(21) Cragel, J., Jr.; Pett, V. B.; Glick, M. D.; DeSimone, R. E. *Inorg. Chem.* **1978**, *17*, 2885–2893.

(22) Baird, M. C.; Wilkinson, G. *J. Chem. Soc. A* **1967**, 865–872.

(23) van Gaal, H. L. M.; Verlaan, J. P. J. *J. Organomet. Chem.* **1977**, *133*, 93–105.

(24) Werner, H.; Kolb, O. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 865–866.

(25) Gaffney, T. R.; Ibers, J. A. *Inorg. Chem.* **1982**, *21*, 2851.

(26) Rakowski DuBois, M.; VanDerveer, M. C.; DuBois, D. L.; Haltiwanger, R. C.; Miller, W. K. *J. Am. Chem. Soc.* **1980**, *102*, 7456–7461.

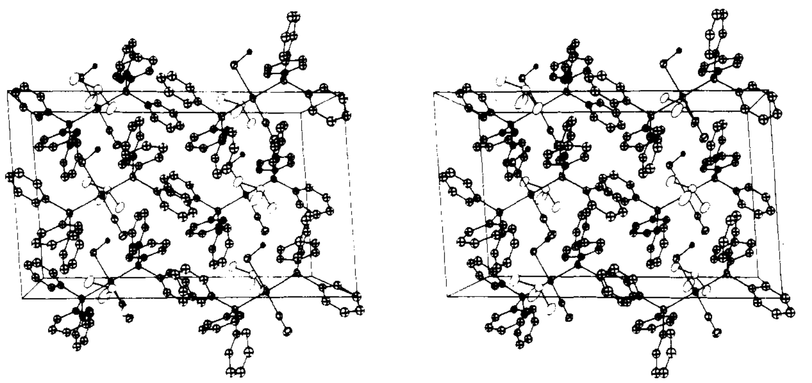


Figure 2. Stereodrawing of the unit cell of *trans*-$Rh(SH)(CO)(PPh_3)_2{\cdot}CHCl_3$. The 50% probability ellipsoids are shown. The mercapto hydrogen atom is shown at the position deduced from the difference electron density map. Other hydrogen atoms are omitted for the sake of clarity. The view is approximately down the y axis.

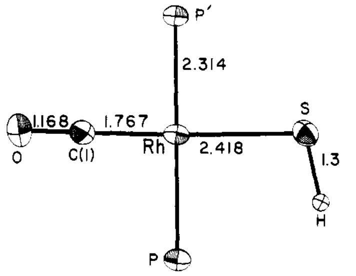
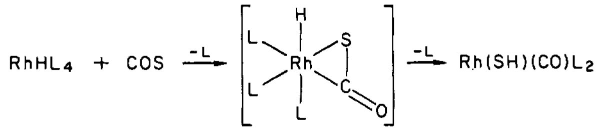


Figure 3. Inner coordination sphere of *trans*-$Rh(SH)(CO)(PPh_3)_2$ with bond distances.

Scheme I. Possible Pathway to the Formation of $Rh(SH)(CO)L_2$



in COS are competitive with simple insertions. Presumably, the weakening of the C=S bond upon coordination of COS to the metal center, which is thought to be the first step in related heteroallene insertion reactions,[1] results in C=S bond cleavage.

The reactions[2-5] of metal amides with CO_2 are believed to involve initial formation of HO_2CNR_2 and subsequent reaction with the metal complex.[4] For the related reactions of metal amides with COS to form monothiocarbamates, no decarbonylation is observed.[2-5] But since formation of the monothiocarbamate ligand would be expected to occur prior to attachment of COS to the metal center, metal-promoted C=S bond cleavage would not be expected in these reactions.

This formal sulfur-insertion reaction observed here for COS contrasts with the reactions of $RhH(PPh_3)_4$ with CO_2 and CS_2. The complex $RhH(PPh_3)_4$ reacts very slowly with CO_2 to afford a carbonate-bridged dimer $Rh_2(CO_3)(PPh_3)_5$.[28] Although this reaction may also involve cleavage of the heteroallene bond (C=O) to form the carbonate ligand, it may also depend on the presence of adventitious water.[28] The complex $RhH(PPh_3)_4$ reacts rapidly with CS_2, but the analogous thiocarbonyl complex, $Rh(SH)(CS)(PPh_3)_2$, does not appear to be produced as we detect no CS stretch in the infrared spectrum of the products. These products are currently being characterized.

Even from the limited number of reactions of metal hydrides with COS that have been reported it is apparent that insertion,[8] carbonylation,[9] and sulfur-abstraction reactions occur readily. The reaction of $RhH(PPh_3)_4$ with COS involves both carbonylation and sulfur abstraction, and unlike other reactions that involve sulfur abstraction from COS, no oxidation of the metal occurs.

Table V. Selected Distances (Å) and Angles (Deg) in $Rh(SH)(CO)(PPh_3)_2{\cdot}CHCl_3$

$Rh(SH)(CO)(PPh_3)_2$		$CHCl_3$	
Rh-S	2.418 (3)	C(2)-Cl(1)	1.773 (6)
Rh-C(1)	1.767 (9)	C(2)-Cl(1)′	1.749 (6)
Rh-P	2.314 (1)	C(2)-Cl(2)	1.756 (7)
C(1)-O	1.168 (9)	C(2)-H(2)	0.982 (6)
P-C(11)	1.836 (1)		
P-C(21)	1.840 (2)		
P-C(31)	1.834 (1)		
Rh-C(1)-O	177.8 (6)	Cl(1)-C(2)-Cl(1)′	109.3 (4)
C(1)-Rh-S	178.1 (2)	Cl(1)-C(2)-Cl(2)	111.2 (4)
P-Rh-P′	176.40 (3)	Cl(1)-C(2)-H(2)	110.4 (5)
P-Rh-S	90.11 (5)	Cl(2)-C(2)-Cl(1)′	109.6 (4)
P′-Rh-S	89.79 (5)	Cl(2)-C(2)-H(2)	108.1 (5)
P-Rh-C(1)	88.3 (2)	Cl(1)′-C(2)-H(2)	108.3 (5)
P′-Rh-C(1)	91.8 (2)		

Table VI. Metal-Mercapto Distances in Metal-Mercaptide Complexes

compd	M coord no.	ligand trans to SH	M-S, Å	ref
$[Ni(SH)(n_2p_2H)][BPh_4]$[a]	4	NR_3	2.144 (3)	18
$[Fe(SH)(pp_3)][BPh_4]$[b]	5	PR_3	2.247 (5)	19
$[Ni(SH)(pp_3)][BPh_4]$	5	PR_3	2.256 (4)	19
cis-$Pt(SH)_2(PPh_3)_2$	4	PR_3	2.340 (2)	20
		PR_3	2.360 (2)	20
trans-$Rh(SH)(CO)(PPh_3)_2$	4	CO	2.418 (3)	this work
$[MoO(SH)16\text{-ane}[S_4]][CF_3SO_3]$[c]	6	O^{2-}	2.486 (1)	21

[a] n_2p_2 = *N,N*-bis(2-(diphenylphosphino)ethyl)-2-(diethylamino)-ethylamine. [b] pp_3 = tris(2-(diphenylphosphino)ethyl)phosphine. [c] Mercapto(1,5,9,13-tetrathiacyclohexadecane)oxomolybdenum(IV) trifluoromethanesulfonate.

Acknowledgments. This work was supported by the National Science Foundation (Grant CHE 80-09671). We thank Johnson-Matthey, Inc., Malvern, PA, for the loan of the rhodium trichloride used in this study.

Registry No. *trans*-$Rh(SH)(CO)(PPh_3)_2{\cdot}CHCl_3$, 81178-18-9; $RhH(PPh_3)_4$, 27497-56-9.

Supplementary Material Available: Tables II–IV giving thermal parameters, calculated positions of the phenyl and chloroform hydrogen atoms, and a listing of the observed and calculated structure amplitudes, respectively (22 pages). Ordering information is given on any current masthead page.

---

(27) Formal sulfur insertions into metal–hydride bonds are known. See: Beck, W.; Danzer, W.; Höfer, R. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 77–78. Beck, W.; Danzer, W.; Thiel, G. *Ibid.* **1973**, *12*, 582.

(28) Krogsrud, S.; Komiya, S.; Ito, T.; Ibers, J. A.; Yamamoto, A. *Inorg. Chem.* **1976**, *15*, 2798–2805.