Inorg. Chem. **1992**, *31*, 4601–4605

Hydrido Mercapto and Bis(mercapto) Derivatives of Ruthenium(II) Phosphine Complexes

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Received April 17, 1992

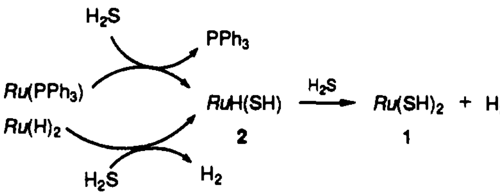
The complex *cct*-$Ru(SH)_2(CO)_2(PPh_3)_2$ (**1**), synthesized by treating THF solutions of $Ru(CO)_2(PPh_3)_3$ or *cct*-$Ru(H)_2(CO)_2(PPh_3)_2$ with H_2S, crystallizes in the space group $P\bar{1}$ (No. 2), with $a = 10.3030$ (6) Å, $b = 22.895$ (13) Å, $c = 12.467$ (4) Å, $\alpha = 119.67$ (3)°, $\beta = 106.23$ (4)°, $\gamma = 117.44$ (4)°, and $Z = 2$; the structure refined to $R = 0.0461$ and $R_w = 0.0519$ for 4283 reflections with $I > 0$. The mercapto protons are located (albeit with large errors) and are not involved in SH/π interactions with the phenyl rings. The H/D exchange reactions of **1** and *cct*-$RuH(SH)(CO)_2(PPh_3)_2$ with CD_3OD are studied and mechanisms suggested. A mixture of *cis*- and *trans*-$Ru(H)_2(dppm)_2$ (dppm = bis(diphenylphosphino)methane) reacts with H_2S to give solely *trans*-$RuH(SH)(dppm)_2$ (**3**), which then reacts more slowly with H_2S to give *cis*- and *trans*-$Ru(SH)_2(dppm)_2$.

Introduction

The interaction of transition metal complexes with H_2S is important in the biological sulfur cycle, in the formation of ores, in hydrodesulfurization catalysis, and in potential routes to the recovery of H_2 from H_2S. Studies in transition metal complex/H_2S chemistry can be traced through recent references.[2–6] Complexes containing coordinated H_2S are rare, and indeed only very recently has an H_2S complex been characterized crystallographically;[4] this was the ruthenium(II) complex $Ru(SH_2)(PPh_3)$('S_4'), where 'S_4' is the tetradentate 2,2′-(ethylenedithio)bis(thiophenolate) dianion. Oxidative addition of H_2S at a metal center is a much more common reaction,[2,3,7] but formation of monomeric mercapto complexes is uncommon, in part because of their instability with respect to deprotonation and conversion to bridged-sulfide species, and, as a result, there are few structural studies reporting on terminal mercapto complexes.[8]

We have noted[2,9] the formation of *cct*-$Ru(SH)_2(CO)_2(PPh_3)_2$ (**1**) (*cct* = *cis*, *cis*, *trans*), via a hydrido mercapto precursor **2**, in reactions outlined in eq 1 (*Ru* = $Ru(CO)_2(PPh_3)_2$).

We now describe here the synthetic details for **1** as well as its structural determination, which, to our knowledge, is the first described for a mononuclear, Ru–mercapto complex; the data allow for direct comparison with those for the analogous dithiolato species *cct*-$Ru(SC_6H_4pMe)_2(CO)_2(PPh_3)_2$, which we reported on recently.[2] Also described here are H/D exchange reactions of **1** and **2** in CD_3OD and the formation of $RuX(SH)(dppm)_2$ species (X = H, SH; dppm = $Ph_2PCH_2PPh_2$) via reaction of a mixture of *cis*- and *trans*-$Ru(H)_2(dppm)_2$ species[10] with H_2S.



(1)

Experimental Section

All the Ru complexes were synthesized from $RuCl_3{\cdot}3H_2O$, donated by Johnson Matthey Ltd. The complexes $Ru(CO)_2(PPh_3)_3$,[11] *cct*-$Ru(H)_2(CO)_2(PPh_3)_2$,[11] and *cct*-$RuH(SH)(CO)_2(PPh_3)_2$[2] were prepared by published methods; $Ru(H)_2(dppm)_2$ was synthesized as a mixture of the cis and trans isomers from Ru(cod)(cot) (cod = cycloocta-1,5-diene, cot = cycloocta-1,3,5-triene)[12] as described by Chaudret et al.[10] Other materials (chemicals, solvents) used and general experimental procedures have been described recently.[2] All NMR spectra were recorded on a Varian XL-300 at room temperature (rt), unless noted otherwise (300 or 121 MHz for ^1H or ^{31}P nuclei, respectively), all ^{31}P spectra being ^1H broad-band decoupled; shifts are externally referenced to TMS in C_6D_6 or aqueous 85% H_3PO_4, respectively, downfield being positive. The solvent provided the deuterium lock signal.

Note that H_2S is extremely toxic and all experimentation involving this reagent should be carried out in a well-vented fume hood.

***cis,cis,trans*-$Ru(SH)_2(CO)_2(PPh_3)_2$ (1).** $Ru(CO)_2(PPh_3)_3$ (400 mg, 0.42 mmol) or *cct*-$Ru(H)_2(CO)_2(PPh_3)_2$ (400 mg, 0.6 mmol) in THF (25 mL) was stirred under H_2S (1 atm) overnight at rt. The solvent was reduced to 10 mL by vacuum transfer, and hexanes (150 mL) was added

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Table I. Crystallographic Data for *cct*-$Ru(SH)_2(CO)_2(PPh_3)_2$

formula	$C_{38}H_{32}O_2P_2RuS_2$	V, Å^3	1706 (1)
fw	747.82	Z	2
space group	$P\bar{1}$, No. 2	T, °C	23
a, Å	10.3030 (6)	ρ_{calc}, g/cm^3	1.456
b, Å	22.895 (13)	ρ_{obs}, g/cm^3	1.47 (1)
c, Å	12.467 (4)	linear abs coeff, cm^{-1}	6.00
α, deg	119.67 (3)	$R(F)$	0.0461
β, deg	106.23 (4)	$R_w(F)$	0.0519
γ, deg	117.44 (4)		

to precipitate the yellow product (75%). Crystals of **1** were prepared by diffusion of hexanes into a concentrated THF solution of the compound.

X-ray Crystallographic Analysis of 1. A roughly cubic crystal was chosen; precession photographs showed no symmetry, and a Delaunay reduction revealed no hidden symmetry. Unit cell parameters were obtained from a least-squares fit of χ, ϕ, and 2θ for 15 reflections in the range $20.3° < 2\theta < 27.7°$ recorded on a Nicolet P3 diffractometer with use of Mo Kα radiation ($\lambda = 0.710\,69$ Å). Some details of the collection are given in Table I; others are given in Table SI.[13] The density was obtained by suspension in an acetone–CCl_4 mixture. Intensities were measured on the same diffractometer wtih a coupled θ(crystal)–2θ-(counter) scan. The methods of selection of scan rates and initial data treatment have been described.[14] Corrections were made for Lorentz and polarization effects but not for absorption. This will make a maximum error in F_o of <1.9%.

The Ru atom was found from a three-dimensional Patterson map, and refinement and electron density difference syntheses revealed all the other atoms. At this stage, the temperature factors of the Ru and the six atoms joined directly to it were made anisotropic. All other atoms were given isotropic temperature factors. Hydrogen atoms were located from the difference map and were refined. Further refinement by full-matrix least squares, which minimized $\sum(|F_o| - |F_c|)^2$, varied all parameters and was terminated when the maximum shift/error was roughly 0.1. Corrections were made for secondary extinction by the SHELX method.[15] Scattering curves were from ref 16, as were the anomalous dispersion corrections applied to the scattering curves for Ru, P, and S.[17] The atom parameters are listed in Table II.[18] Selected bond lengths and angles are given in Table III. Anisotropic thermal parameters, H atom parameters, and bond lengths and angles within the phenyl groups are included as supplementary material (Tables SII–SIV, respectively).[13]

Reactions of *cct*-$Ru(H)_2(CO)_2(PPh_3)_2$, *cct*-$Ru(SH)_2(CO)_2(PPh_3)_2$ (1), and *cct*-$RuH(SH)(CO)_2(PPh_3)_2$ (2) with CD_3OD. A 40 mM C_6D_6 solution of the complex was prepared under Ar, and a ^{1}H NMR spectrum was acquired while the probe temperature equilibrated. Enough CD_3OD was then injected to make a 4% v/v CD_3OD/C_6D_6 mixture. The intensities of the peaks in the ^{1}H NMR spectra were then observed with successive acquisitions using constant experimental parameters.

***trans*-$RuH(SH)(dppm)_2$ (3).** A sample of $Ru(H)_2(dppm)_2$ (6.0 mg, 6.9 μmol) was dissolved in C_6D_6 (0.5 mL) under Ar in a septum-capped NMR tube which was subsequently flushed with H_2S. After a 45-min reaction time at rt, complete converion to species **3** was apparent. ^{1}H NMR (C_6D_6): δ −9.46 (qn, $^2J_{PH}$ = 19 Hz, Ru–H), −3.55 (br, Ru–SH), 4.54 (dt, $^2J_{HH}$ = 16, $^2J_{PH}$ = 3 Hz, CH_2), 5.21 (m, CH_2). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 0.40 (s).[19]

Table II. Atomic Positional Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3)

atom	x	y	z	U_{eq}^{a} or U_{iso}
Ru	847.6 (5)	227.01 (2)	3504.6 (4)	11.1^a
P1	474 (2)	2210 (1)	5283 (1)	11.9^a
P2	1019 (2)	2319 (1)	1651 (1)	12.3^a
S1	2146 (2)	3892 (1)	5210 (2)	19.6^a
S2	−2544 (2)	1461 (1)	1904 (2)	18.0^a
C1	40 (8)	1073 (4)	2239 (6)	20^a
O1	−350 (8)	390 (3)	1532 (5)	18^a
C2	3452 (8)	2909 (4)	4816 (6)	36^a
O2	4986 (6)	3274 (3)	5603 (5)	28^a
C11	2692 (6)	2914 (3)	7256 (5)	31 (1)
C12	2763 (8)	2573 (4)	7916 (6)	45 (1)
C13	4419 (8)	3173 (4)	9485 (7)	54 (1)
C14	6028 (9)	4115 (4)	10405 (8)	55 (2)
C15	5984 (9)	4464 (4)	9767 (7)	54 (1)
C16	4316 (7)	3864 (4)	8201 (6)	44 (1)
C21	−567 (6)	2601 (3)	6014 (5)	32 (1)
C22	−1016 (7)	3011 (3)	5699 (6)	39 (1)
C23	−1728 (8)	3324 (4)	6340 (7)	52 (1)
C24	−2035 (8)	3216 (4)	7252 (7)	56 (2)
C25	−1622 (8)	2798 (4)	7553 (7)	54 (2)
C26	−861 (8)	2501 (4)	6961 (6)	45 (1)
C31	−1157 (6)	963 (3)	4245 (5)	32 (1)
C32	−536 (7)	523 (4)	4052 (6)	40 (1)
C33	−1833 (8)	−445 (4)	3132 (7)	50 (1)
C34	−3746 (9)	−987 (5)	2390 (7)	56 (2)
C35	−4400 (9)	−568 (4)	2536 (7)	54 (2)
C36	−3114 (7)	402 (4)	3451 (6)	41 (1)
C41	3304 (6)	2732 (3)	2154 (5)	30 (1)
C42	3327 (8)	2053 (4)	1294 (7)	44 (1)
C43	5074 (8)	2347 (4)	1797 (7)	56 (2)
C44	6820 (8)	3320 (4)	3131 (7)	52 (1)
C46	5070 (7)	3704 (4)	3507 (6)	43 (1)
C51	950 (6)	3110 (3)	1667 (5)	31 (1)
C52	2233 (8)	3751 (4)	1742 (6)	46 (1)
C53	2052 (9)	4311 (4)	1701 (7)	56 (2)
C54	619 (8)	4234 (4)	1581 (7)	55 (1)
C55	−709 (8)	3583 (4)	1458 (6)	47 (1)
C56	−536 (7)	3025 (4)	1510 (6)	41 (1)
C61	−783 (6)	1198 (3)	−565 (5)	33 (1)
C62	−653 (8)	1262 (4)	−1590 (7)	50 (1)
C63	−1907 (9)	429 (4)	−3261 (7)	59 (2)
C64	−3293 (9)	−455 (5)	−3914 (8)	55 (2)
C65	−3464 (9)	−539 (4)	−2948 (7)	53 (1)
C66	−2218 (7)	293 (4)	−1249 (6)	43 (1)

^{a} $U_{eq} = {}^1/_3(U_{11} + U_{22} + U_{23} + 2U_{12}\cos\gamma + 2U_{13}\cos\beta + 2U_{23}\cos\alpha)$.

Table III. Selected Interatomic Distances (Å) and Angles (deg)

Ru–P1	2.411 (1)	Ru–P2	2.418 (2)	Ru–S1	2.472 (2)
Ru–S2	2.470 (2)	Ru–C1	1.891 (8)	Ru–C2	1.891 (7)
P1–C11	1.846 (6)	P1–C21	1.846 (8)	P1–C31	1.832 (6)
P2–C41	1.835 (7)	P2–C51	1.836 (9)	P2–C61	1.841 (4)
C1–O1	1.12 (1)	C2–O2	1.12 (1)	S1–H1	1.0 (2)
S2–H2	1.2 (1)				

P1–Ru–P2	175.57 (7)	P1–Ru–S1	91.0 (1)	P1–Ru–S2	85.4 (1)
P1–Ru–C1	91.2 (2)	P1–Ru–C2	92.0 (1)	P2–Ru–S1	87.5 (1)
P2–Ru–S2	90.5 (1)	P2–Ru–C1	90.6 (2)	P2–Ru–C2	92.1 (1)
S1–Ru–S2	92.2 (1)	S1–Ru–C1	175.6 (2)	S1–Ru–C2	86.9 (2)
S2–Ru–C1	91.8 (2)	S2–Ru–C2	177.3 (1)	C1–Ru–C2	89.1 (2)
Ru–P1–C11	117.1 (1)	Ru–P1–C21	120.3 (1)	Ru–P1–C31	109.9 (1)
C11–P1–C21	99.7 (3)	C11–P1–C31	105.1 (3)	C21–P1–C31	102.8 (3)
Ru–P2–C41	108.5 (3)	Ru–P2–C51	117.1 (2)	Ru–P2–C61	120.0 (3)
C41–P2–C51	106.3 (3)	C41–P2–C61	102.0 (3)	C51–P2–C61	101.1 (3)
Ru–C1–O1	176.8 (7)	Ru–C2–O2	178.1 (9)	Ru–S1–H1	84 (12)
Ru–S2–H2	99 (14)				

***cis*- and *trans*-$Ru(SH)_2(dppm)_2$ (4).** In situ samples of **3** (see above) or solutions of $Ru(H)_2(dppm)_2$ under H_2S, on heating to 60 °C (e.g., in the NMR probe) for 1.5 h, generated a mixture of *cis*- and *trans*-**4**. Such a mixture was precipitated on reacting $Ru(H)_2(dppm)_2$ (300 mg, 0.34 mmol) with H_2S (1 atm) in THF (30 mL) for 24 h at rt. Anal. Calcd for $C_{50}H_{46}P_4RuS_2$: C, 64.16; H, 4.95. Found: C, 63.61; H, 4.98. This precipitate contained 5% of *trans*-**4**, while further product precipitated from the filtrate by addition of hexanes contained 33% of the trans isomer. Although the C analysis of 0.55% low, the NMR data leave no doubt in identification of the sample.

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[13] Supplementary material.

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[18] All computations were carried out on a CYBER 170/815 computer. Programs used for initial data treatment were from the XRAY76 package (Stewart, J. M. *Technical Report TR-446*; University of Maryland: College Park, MD, 1976). The structure was solved with use of SHELX.[15] Planes were calculated with NRC-22 (Ahmed, F. R.; Rippy, M. E. *NRC-22*; National Research Council of Canada: Ottawa, Canada, 1978). Diagrams were prepared from ORTEPII (Johnson, C. K. *Report ORNL-5138*; Oak Ridge National Laboratory: Oak Ridge, TN, 1976).

[19] Abbreviations used in NMR spectra: s = singlet, d = doublet, t = triplet, qn = quintet, b = broad, m = multiplet.

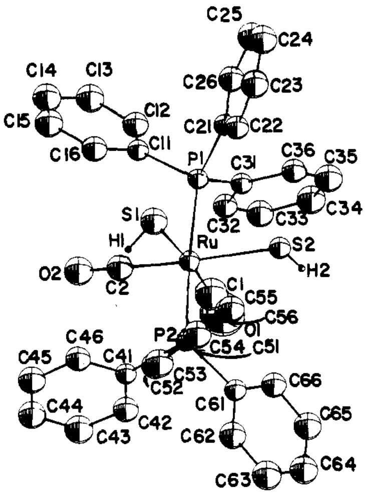

Figure 1. Molecule of *cct*-$Ru(SH)_2(CO)_2(PPh_3)_2$ (1), showing the atom numbering.

***trans*-$Ru(SH)_2(dppm)_2$.** ^1H NMR (C_6D_6): δ -3.73 (qn, $^3J_{PH}$ = 5.7 Hz, SH), 5.10 (m, CH_2). $^{31}P\{^1H\}$ NMR (C_6D_6): δ -7.05 (s).

***cis*-$Ru(SH)_2(dppm)_2$.** ^1H NMR (C_6D_6): δ -1.92 (m, SH), 4.62 (m, CH_2), 5.10 (m, CH_2). $^{31}P\{^1H\}$ NMR (C_6D_6): δ -5.93 (t, $^2J_{PP}$ = 28.5 Hz), -22.65 (t, $^2J_{PP}$ = 28.5 Hz).

Results and Discussion

Structure of *cct*-$Ru(SH)_2(CO)_2(PPh_3)_2$ (1). The identity of **1** was established previously by elemental analysis and IR and NMR spectroscopy,[2] and the solid-state structure (Figure 1) now confirms this formulation. The mercapto protons are located, although the error in bond lengths and angles is high; the S–H bond lengths (1.0 (2) and 1.2 (1) Å) are shorter than found in gaseous H_2S (1.33 Å)[20] and in the few terminal mercapto complexes with located protons (1.2–1.4 Å).[8a,b,d] The S–H distances in $Ru(SH_2)(PPh_3)$('S_4') (see Introduction) are 1.21 and 1.19 Å, although the H atoms are strongly H-bonded, via intermolecular interactions, with respectively the O atom of a THF solvate and an S atom of an 'S_4' ligand.[4]

The Ru–S–H bond angles (84 (12) and 99 (14)°) straddle the expected value[21] of about 94°. These angles are smaller than the Ru–S–C bond angles (113°) in the analogous complex *cct*-$Ru(SC_6H_4pMe)_2(CO)_2(PPh_3)_2$ (**5**),[2] a result that parallels the angles found at sulfur in H_2S (92.1°)[20] and (p-$MeC_6H_4)_2S$ (109°);[22] the larger angles in the thioether and **5** can be attributed to electronic factors (the possibility of multiple bonding between the S and sp^2 C atom, coupled with greater s orbital contribution to hybridization of the S atom[23]) as well as obvious steric factors. Reports of M–S–H angles in terminal mercapto ligands are rare; an unrefined one in *trans*-$Rh(SH)(CO)(PPh_3)_2$ is given as 100°,[8d] while such angles in the pseudotetrahedral complex $(C_5Me_5)_2Ti(SH)_2$ are 106 and 116°, possibly because more electropositive atoms attached to sulfur cause wider angles at the S.[24] The bridging mercapto ligands in $[\{MeC(CH_2PPh_2)_3\}RhH(\mu\text{-}SH)]_2$ have Rh–S–H angles of 92 (6)°, comparable to the values in **1**.[25]

In **1**, the closest approach of an SH proton to a phenyl C is 3.17 Å (for H1–C66), greater than the sum (2.99 Å) of the van der Waals radii for the two atoms. Shorter corresponding distances of 2.63 and 2.69 Å were reported[8b] for two of the bridging SH groups and phenyl C atoms in the complex $(PhMe_2P)_3Ru(\mu\text{-}SH)_3Ru(SH)(PMe_2Ph)_2$, and on the basis of these findings and related data within $[Fe(ppp)]_2(\mu\text{-}SH)_3^+$ (ppp = bis[2-(diphenylphosphino)ethyl]phenylphosphine),[26] and for the terminal –SH group of *trans*-$Rh(SH)(CO)(PPh_3)_2$,[8d] Osakada et al.[8b] suggested that HS–M–P–Ph structures (M = Fe, Ru, Rh) satisfy structural and electronic requirements for SH/π interactions. The data for **1** show that this is not always the case. The point has relevance in hydrodesulfurization mechanisms, where reactions between mecapto protons and thiophene rings have been suggested.[27]

The unusually small S–S distance (3.26 Å) and S–Ru–S angle (83.05°) observed in the dithiolato complex **5**, which result from the bulkiness of the aryl groups,[2] are not evident in **1** (3.56 Å, 92.2°). In the other reported structure for a cis-dimercapto species, in the square-planar $Pt(SH)_2(PPh_3)_2$, the SH ligands are more constrained (S–S = 3.12 Å, S–Pt–S = 83.2°).[8e]

The lengths of the Ru–S bonds (trans to CO) in **1** (2.472, 2.470 Å) are similar to those in **5** (2.450, 2.470 Å)[2], showing that a change from a thiolate to a mercapto group has little effect on the metal–sulfur bond length. Shorter Ru^{II}–S bonds (2.40–2.43 Å)[2,28] are found in complexes with thiolato ligands trans to weaker π acceptors than CO, such as a phosphine or thiolate group; in $(PhMe_2P)_3Ru(\mu\text{-}SH)_3Ru(SH)(PMe_2Ph)_2$, the Ru–S bond with the terminal SH ligand is trans to a bridging SH ligand and has a bond length of 2.44 Å.[8b] The Ru–C and C–O bond lengths within **1** (1.89, 1.12 Å) are similar to those in carbonyl ligands trans to thiolates[2,28] and carboxylates[29] in other Ru(II) complexes, including **5**. The Ru–P distances (2.411, 2.418 Å) are significantly shorter than those in **5** (average 2.446 Å), presumably because the mercapto ligands are less bulky than the thiolato ligands. Substitution reactions of **1** and **5** (for example, exchange of the PPh_3 or $SH^-/SC_6H_4pMe^-$ ligands) occur via a rate-determining loss of the phosphine, and the much slower rates for **1**[30] reflect the shorter Ru–P distances.

The rings on each phosphine are twisted so that there is a marked distortion from local C_3 symmetry for each phosphine. The C2*i* (*i* = 1–6) ring is almost coplanar with Ru,P1,C21 (dihedral angle 5.1 (3)°), and the C1*i* ring has a normal twist (dihedral angle with Ru,P1,C11 = 44.8 (3)°) whereas ring C3*i* is almost at right angles to Ru,P1,C31 (100.8 (2)°). Similar effects are seen on the second phosphine where the dihedral angles are C4*i*,Ru,P2,C41 = 81.6 (2)°, C5*i*,Ru,P2,C51 = 59.7 (3)°, and C6*i*,Ru,P2,C61 = 3.8 (4)°. These distortions appear to be caused primarily by intramolecular interactions of the rings with the equatorial ligands, since, as can be seen in Figure 2, only the C4*i* rings show any sign of packing to maximize any π–π interactions with its centrosymmetrically related neighbor.

As can be seen in Figure 2, the packing is not dominated by any strong interactions. Besides the lack of π–π interactions there is no evidence of any hydrogen bond involving the SH group and all intermolecular distances are greater or equal to van der Waals distances.

Deuterium Exchange Reactions. The mercapto protons of *cct*-$RuX(SH)(CO)_2PPh_3)_2$ (X = SH (**1**), H (**2**)) undergo deuterium exchange with 4% (v/v) CD_3OD in C_6D_6 (Figures 3 and 4). The mechanism is unlikely to involve replacement of a PPh_3 ligand by CD_3OD, followed by intramolecular exchange, because, for example, the H/D exchange for **1** ($t_{1/2}$ ~ 300 s; Figure 3) is much faster than loss of the PPh_3 ligand ($t_{1/2}$ ~ 1800 s; see

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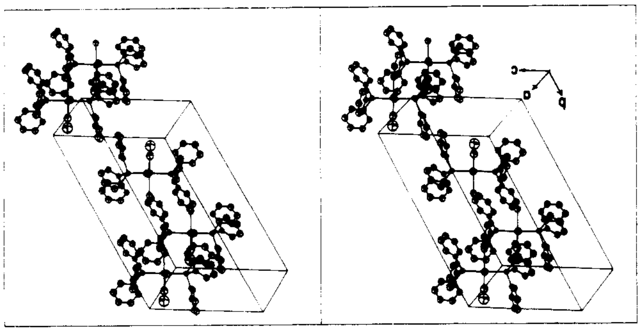


Figure 2. Packing of the molecules of 1 within the unit cell.

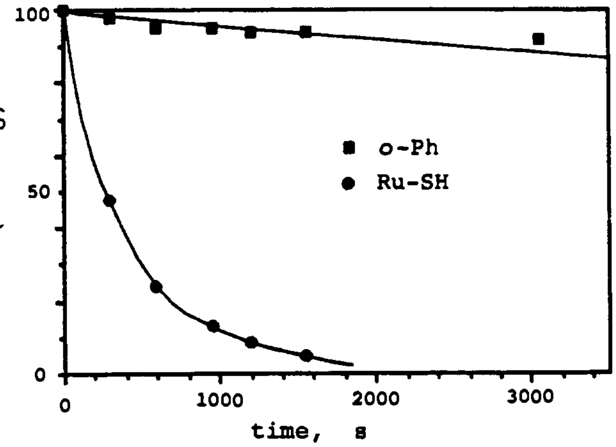


Figure 3. Time dependence of the intensity of the ^1H NMR signals of *cct*-$Ru(SH)_2(CO)_2(PPh_3)_2$ (**1**) (3.3 mM) in 4% v/v CD_3OD/C_6D_6 at 25 °C: δ(Ru–SH) −1.97 t, $^3J_{PH}$ = 6.8 Hz; δ(Ph) 8.14 m (*o*-H). NMR data for **1** were reported previously.[2] A standard first-order log plot gives a rate constant of 2.3×10^{-3} s^{-1} for the mercapto hydride exchange process.

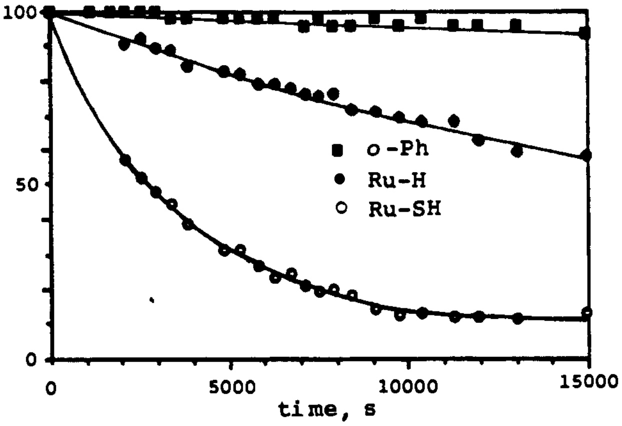
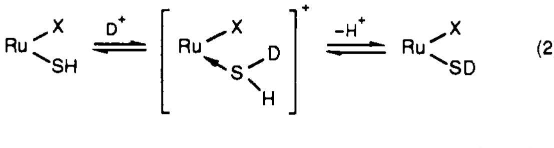
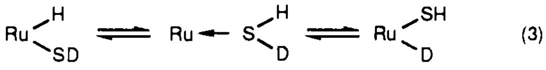


Figure 4. Time dependence of the intensity of the ^1H NMR signals of *cct*-$RuH(SH)(CO)_2(PPh_3)_2$ (**2**) (4.4 mM) in 4% v/v CD_3OD/C_6D_6 at 19 °C: δ(Ru–H) −4.83 dt, $^2J_{PH}$ = 20.1, $^3J_{HH}$ = 3.1 Hz; δ(Ru–SH) −3.01 dt, $^3J_{PH}$ = 4.9, $^3J_{HH}$ = 2.6 Hz; δ(Ph) 7.91 m (*o*-H). NMR data for **2** were reported previously.[2] Standard first-order log plots give rate constant values of 2.9×10^{-4} and 4.1×10^{-5} s^{-1}, respectively, for the mercapto hydride and hydrido ligand exchange processes.

above).[30] A reasonable mechanism is deuteration/deprotonation of the SH ligand (eq 2), but other mechanisms (e.g. involving the interchange of hydrogens between hydrogen-bonded oligomers) cannot be ruled out.

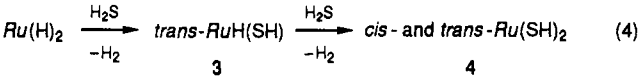


The exchange at the hydride of **2** occurs more slowly than that at the mercapto moiety (Figure 4). Intermolecular exchange of the hydride with D$^+$ is unlikely because *cct*-$Ru(H)_2(CO)_2(PPh_3)_2$ (δ(Ru–H) −6.34 t, J_{PH} = 23.4 Hz) shows no exchange in 4% CD_3OD in C_6D_6 at rt even after 2 h. Using Morris's extension[31] of Lever's ligand additivity (a ligand electrochemical series),[32] we can predict that the η^2-H_2 complexes which would result from protonation of the hydride ligands of the dihydride or **2** would have pK_a values < −3 or 0, respectively, and so neither hydride is sufficiently basic to be easily protonated by alcohol; more basic hydrides such as $Ru(H)_2(dppm)_2$[33] and $Fe(H)_2(dmpe)_2$, dmpe = 1,2-bis(dimethylphosphino)ethane,[34] do undergo exchange with deuterated alcohols. More likely for **2** is an intramolecular process of exchange with the mercapto proton, as suggested by Osakada et al.[35] for $RuH(SH)(PPh_3)_3$.



Of note is the much slower exchange between CD_3OD and the *o*-phenyl protons of **1** and **2**, as evidenced by decreasing intensity of the *o*-H signals relative to the *m*- and *p*-H signals (Figures 3 and 4); this slower exchange, observed also within $RuH(SH)(PPh_3)_3$,[35] requires an orthometalated intermediate, a precondition for this being at least one vacant site cis to a coordinated PPh_3. The demonstrated slow loss of PPh_3 from **1** in some substitution reactions[30] could accommodate an orthometalation mechanism, at least for this species. Alternatively, particularly for **2**, a less likely reversible elimination of H_2S coupled with exchange between H_2S and CD_3OD would allow for formation of a coordinatively unsaturated intermediate and orthometalation, as well as further exchange pathway for the hydrido and mercapto ligands.

Reaction of *cis*- and *trans*-$Ru(H)_2(dppm)_2$ with H_2S. *cis*- and *trans*-$Ru(H)_2(dppm)_2$, readily distinguished by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, and always isolated as a 4:1 mixture,[10] react with H_2S at rt to form in situ solely *trans*-$RuH(SH)(dppm)_2$ (**3**), while, at higher temperatures, *cis*- and *trans*-$Ru(SH)_2(dppm)_2$ (**4**) are formed via **3** (eq 4, *Ru* = $Ru(dppm)_2$; **4** is isolated as a mixture of the cis and trans isomers; the H_2 produced in both stages of the overall reaction is readily detected at δ 4.46 ppm in the ^1H NMR spectra.



$$\mathit{Ru}(H)_2 \xrightarrow[-H_2]{H_2S} \underset{\mathbf{3}}{trans\text{-}\mathit{Ru}H(SH)} \xrightarrow[-H_2]{H_2S} \underset{\mathbf{4}}{cis\text{- and }trans\text{-}\mathit{Ru}(SH)_2} \qquad (4)$$

Complex **3** is characterized as the trans isomer by the high-field hydride quintet in the ^1H NMR (δ −9.46, with the $^2J_{PH}$ value consistent with phosphines cis to the hydride[2,10]) and the singlet in the $^{31}P\{^1H\}$ NMR. The mercapto proton appears as a broad peak at δ −3.55, although it should be noted that the integral intensity is only about 30% that of the hydride, presumably due to a long T_1 value of the SH proton; a similar observation is seen within the ^1H NMR spectrum of *cct*-$RuH(SH)(CO)_2(PPh_3)_2$. The ^1H NMR spectrum of **4** shows a high-field SH quintet at δ −3.73 with cis coupling to four equivalent P atoms, attributed to the trans isomer, while a complex multiplet at δ −1.92 is attributed to *cis*-**4**; the methylene signal appears at δ 5.10 for *trans*-**4** while the cis isomer has methylene multiplets at δ 4.62 and also at δ 5.10. The $^{31}P\{^1H\}$ spectra contain the expected singlet for *trans*-**4** and two triplets for *cis*-**4**. The cis/trans composition of isolated **4** was variable depending on the solvent used and reaction conditions (for example, see Experimental

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(33) The hydride ligands of both *cis*- and *trans*-$Ru(H)_2(dppm)_2$ undergo complete D-exchange with 4% CD_3OD in C_6D_6 in < 25 min at rt.

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Section), implying that the interconversion between the isomers is relatively slow in solution. Under NMR conditions, **3** at 60 °C under 1 atm of H_2S converts to a 1:2 mixture of *cis*- and *trans*-**4** with pseudo-first-order behavior ($t_{1/2}$ = 1200 s).

Of note, reaction of SH^- with *trans*-$FeCl_2(dmpe)_2$ gives only *trans*-$Fe(SH)_2(dmpe)_2$ (cf. eq 4), which was characterized structurally, although the SH protons were not located;[36] the nondetection of a cis isomer was attributed to steric repulsion between the S lone pairs in such a species, a conclusion that presupposes that the trans isomer is a thermodynamically controlled product. Our findings would then suggest that kinetics, rather than thermodynamics, determine which isomer is produced.

More detailed kinetic studies on the reaction of *cis*- and *trans*-$Ru(H)_2(dppm)_2$ with thiophenol and benzyl mercaptan to give the hydrido thiolato product (cf. eq 4)[30] suggest the mechanism parallels that proposed by Boyd et al.[34] for the reaction of Fe$(H)_2(dmpe)_2$ with thiols, that is via protonation to give a η^2-H_2 intermediate which loses H_2 to generate a coordination site which is subsequently filled by the thiolate ligand. To determine whether H_2S reacts with $Ru(H)_2(dppm)_2$ via an initial protonation step requires kinetic studies on reactions on this dihydride with other protonic, as well as nonprotonic, reagents (e.g. CO).

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support in the form of operating grants (B.R.J., C.J.L.L.) and a postgraduate fellowship (P.G.J.), the Isaak Walton Killam Foundation for a postdoctoral fellowship (C.-L.L.), Johnson Matthey Ltd. for the loan of Ru, and Dr. R. H. Morris, University of Toronto, for useful discussion.

Supplementary Material Available: Tables SI–SIV, listing additional crystallographic details, anisotropic thermal parameters, hydrogen atom parameters, and bond lengths and angles within the phenyl groups (4 pages). Ordering information is given on any current masthead page.

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