direct methods followed by successive applications of Fourier methods. Phenyl hydrogen atoms were placed in calculated fixed positions. Full-matrix least-squares refinement minimizing $\sum w(|F_o| - |F_c|)^2$ converged to the *R* values given in Table I. No extinction correction was applied. A disordered CH_2Cl_2 molecule, well separated from the anionic and cationic portions, was included. Final atomic positional parameters for the refined atoms are included in Table II. Selected bond distances and angles are given in Table III. Other data are included as supplementary material.

Acknowledgment. We thank ARCO Chemical Co. and the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy (Contract DE-FG02-88ER13880), for support of this work. The National Science Foundation provided a portion of the funds for the purchase of the X-ray (Grant CHE-7820347) and NMR (Grant PCM-8115599) equipment.

Supplementary Material Available: Tables of melting point and IR data, full crystallographic data and data collection parameters, fractional coordinates, thermal parameters, and additional distances and angles (6 pages); a listing of structure factors (25 pages). Ordering information is given on any current masthead page.

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Ascertaining the Roles of Each Metal in the Activation of S–H Bonds in Hydrogen Sulfide and Thiols by the Heterobinuclear Complex $[RhRe(CO)_4(Ph_2PCH_2PPh_2)_2]$

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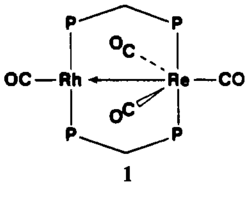
Received December 11, 1989

The reactions of H_2S, HSEt, and HSPh with $[RhRe(CO)_4(dppm)_2]$ have been studied. These reactions are facile at ambient temperature, yielding $[RhRe(CO)_4(\mu\text{-S})(dppm)_2]$ (**2**) in the case of H_2S and $[RhRe(CO)_3(\mu\text{-H})(\mu\text{-SR})(dppm)_2]$ (R = Et (**5**) Ph (**6**)) for the thiols. Monitoring these reactions at −80 °C by ^{31}P, ^{13}C, and ^1H NMR spectroscopy indicates that in all cases the first species is the HSR adduct (R = H, Et, Ph), which then yields $[RhRe(CO)_4(SR)(\mu\text{-H})(dppm)_2]$ via oxidative addition of an S–H bond. In subsequent steps the reactions involving H_2S and thiols proceed differently. In the case of H_2S, the presumed second S–H oxidative addition step is followed by facile H_2 loss, and no additional intermediate is observed before formation of **2**, even at −60 °C. For ethanethiol no other intermediate is observed before formation of **5**; however, for benzenethiol a tetracarbonyl species, in which the hydride ligand has migrated to Re, is observed after the hydride-bridged species, followed by movement of the thiolate group to the bridging position with concomitant loss of one carbonyl to give **6**. Mechanisms for these transformations are proposed. The structure of **5** was determined by X-ray techniques, confirming that the thiolate group and the hydride ligand bridge the metals on opposite faces of the dimer. Compound **5** crystallizes in the monoclinic space group $P2_1/c$ with $a = 12.216$ (3) Å, $b = 19.845$ (7) Å, $c = 23.316$ (7) Å, $\beta = 103.19$ (2) Å, $V = 5503$ Å^3, and $Z = 4$ and has refined to $R = 0.049$ and $R_w = 0.056$ on the basis of 370 parameters varied and 5011 independent observations.

Introduction

The current interest in binuclear complexes is based on the assumption that the presence of the two adjacent metals will give rise to reactivity patterns that differ substantially from those of the mononuclear analogues. With this idea in mind, we have chosen to investigate chemistry that might clearly benefit from the presence of two adjacent metals, and as part of this study, we have been examining the activation of adjacent heteroatom–hydrogen bonds in H_2X molecules (X = S, Se, SiR_2, SiHR).[1,2] We are interested in the initial sites of substrate attack in various binuclear complexes, the involvement of the adjacent metals in X–H bond activation processes, the chemically significant ligand rearrangements that occur, and the possibility of subsequent binuclear reductive elimination reactions. In this paper we present details about the activation of H_2S and thiols. Hydrogen sulfide is of interest to us because of its potential use as a source of H_2[3–6] and organosulfur compounds,[7] whereas thiols may serve to model unstable intermediates both in the initial S–H activation processes involving H_2S and in the subsequent formation of organosulfur products.

Although our initial studies involved homo- and heterobinuclear complexes of Rh and Ir,[1,2] we have recently turned to heterobinuclear complexes in which Rh is combined with an earlier transition metal.[8] The compound of interest in this study, $[RhRe(CO)_4(dppm)_2]$ (**1**) (dppm = $Ph_2PCH_2PPh_2$), has the



1

structure shown, in which a dative bond between the coordinatively saturated Re(−1) center and the unsaturated Rh(+1) center can be formulated.[8] Consistent with the coordinative unsaturation at Rh and the low oxidation states of the metals, compound **1** has been found to be active toward oxidative addition reactions, involving substrates such as H_2, Cl_2, and HCl,[9] and so seemed a good candidate for oxidative addition reactions of H–S bonds in H_2S and thiols. It was hoped that the strong tendency of Re to maintain an 18-electron configuration might allow the characterization of intermediates that were difficult to observe when the second metal was Rh or Ir.[1,2]

In a related study involving the reaction of H_2S with $[Pd_2Cl_2(dppm)_2]$,[3] activation of both H–S bonds followed by facile

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Table I. Spectral Data[a]

compd	IR, cm^{-1} [b]	NMR		
		δ($^{31}P\{^1H\}$)[c]	δ(^1H)[d,e]	δ(^{13}C)[d]
[RhRe(μ-S)(CO)$_4$(dppm)$_2$] (**2**)	1990 (sh), 1953 (st), 1868 (med), 1830 (sh)	22.2 (dm, $^1J_{Rh-P}$ = 134 Hz), −3.6(m)[f]	2.6 (m, 2 H), 4.8 (m, 2 H)[f]	215.8 (m), 193.2 (s), 193.5 (dt, $^1J_{Rh-C}$ = 70 Hz, $^2J_{P(Rh)-C}$ = 15 Hz), 193.8 (b)[f]
[RhRe(H_2S)(CO)$_4$(dppm)$_2$] (**3**)	*h*	11.6 (dm, $^1J_{Rh-P}$ = 146 Hz), −1.4 (m)[i]	4.2 (m, 4 H)[i]	204 (s, 4 C)[i]
[ReRh(CO)$_4$(μ-H)(SH)(dppm)$_2$] (**4**)	*h*	30.8 (dm, $^1J_{Rh-P}$ = 126 Hz), 7.7 (m)[g]	−0.85 (t, 1 H, $^3J_{P(Rh)-H}$ = 15.3 Hz), −11.1 (m, 1 H, $^1J_{Rh-H}$ = 32 Hz, $^2J_{P(Rh)-H}$ = 13 Hz, $^2J_{P(Re)-H}$ = 7 Hz), 3.25 (m, 2 H), 3.7 (m, 2 H)[g]	248 (s), 206 (s), 196 (s), 193 (d, $^1J_{Rh-C}$ = 71 Hz)[g]
[RhRe(CO)$_3$(μ-H)(μ-SEt)(dppm)$_2$] (**5**)	1951 (med), 1923 (st), 1850 (st)	29.8 (dm, $^1J_{Rh-P}$ = 123 Hz), 11.1 (m)[g]	−10.5 (m, 1 H, $^1J_{Rh-H}$ = 20.5 Hz, $^2J_{P(Rh)-H}$ = 10.0 Hz, $^2J_{P(Re)-H}$ = 10.0 Hz), 2.9 (m, 2 H), 4.6 (m, 2 H), 0.0 (t, 3 H), 2.1 (q, 2 H)[g]	197.8 (s, 2 C), 198.1 (dm, 1 C, $^1J_{Rh-C}$ = 77 Hz, $^2J_{P(Rh)-C}$ = 14 Hz)[g]
[RhRe(CO)$_3$(μ-H)(μ-SPh)(dppm)$_2$] (**6**)	1950 (sh), 1922 (st), 1841 (med)	27.5 (dm, $^1J_{Rh-P}$ = 119 Hz), 6.3 (m)[g]	−9.71 (m, 1 H, $^1J_{Rh-H}$ = 22.3 Hz, $^2J_{P(Re)-H}$ = 9.0 Hz, $^2J_{P(Rh)-H}$ = 11.0 Hz), 3.6 (m, 2 H), 3.2 (m, 2 H)[g]	198.8 (s), 197.1 (s), 189.1 (dm, $^1J_{Rh-C}$ = 80 Hz)[g]
[RhRe(HSEt)(CO)$_4$(dppm)$_2$] (**7**)	*h*	11.3 (dm, $^1J_{Rh-P}$ = 145 Hz), −1.4 (m)[i]	4.2 (m, 4 H)[i]	203 (s, 4 C)[i]
[RhRe(CO)$_4$(μ-H)(SEt)(dppm)$_2$] (**8**)	*h*	27.9 (dm, $^1J_{Rh-P}$ = 129 Hz), 8.5 (m)[g]	−11.1 (m, 1 H, $^1J_{Rh-H}$ = 26 Hz), 3.2 (m, 2 H), 3.9 (m, 2 H), 0.1 (t, 3 H), 2.6 (q, 2 H)[g]	246 (s), 206 (s), 197 (s), 193.7 (dm, $^1J_{Rh-C}$ = 68 Hz)[g]
[RhRe(HSPh)(CO)$_4$(dppm)$_2$] (**9**)	*h*	11.7 (dm, $^1J_{Rh-P}$ = 145 Hz), −1.3 (m)[i]	4.2 (m, 4 H)[i]	203 (s, 4 C)[i]
[RhRe(CO)$_4$(μ-H)(SPh)(SPh)(dppm)$_2$] (**10**)	*h*	27.0 (dm, $^1J_{Rh-P}$ = 127 Hz), 8.1 (m)[g]	−11.4 (m, 1 H, $^1J_{Rh-H}$ = 28 Hz), 3.4 (m, 2 H), 3.7 (m, 2 H)[g]	246 (s), 206 (s), 196 (s), 193.4 (dm, $^1J_{Rh-C}$ = 71 Hz)[g]
[RhRe(CO)$_4$(H)(SPh)(dppm)$_2$] (**11**)	*h*	29.1 (dm, $^1J_{Rh-P}$ = 105 Hz), −5.4 (m)[j]	−10.65 (m, 1 H, $^2J_{P(Re)-H}$ = 10.4 Hz), 4.5 (m, 2 H), 4.7 (m, 2 H)[j]	203 (dm, $^1J_{Rh-C}$ = 78 Hz), 201 (s), 194 (s, 2 C)[j]

[a] Abbreviations used: w = weak, med = medium, st = strong, sh = shoulder, s = singlet, m = multiplet, t = triplet, dm = doublet of multiplets, q = quartet, b = broad, dt = doublet of triplets. [b] CH_2Cl_2 solution in KCl cells. [c] Vs 85% H_3PO_4 in CD_2Cl_2. [d] Vs TMS in CD_2Cl_2. [e] Phenyl resonances are not given. [f] Ambient temperatures. [g] −40 °C. [h] IR data not obtained for this labile intermediate. [i] −60 °C. [j] −20 °C.

H_2 loss to yield [Pd_2Cl_2(μ-S)(dppm)$_2$] was observed. However, the mechanistic details necessary to outline the involvement of the metals were not elucidated. In the present study we attempt to address the questions relating to the involvement of the adjacent metals in H–S bond activation.

Experimental Section

General Considerations. All solvents were dried and distilled under argon before use. Sodium–benzophenone was used as a drying agent in all cases except for CH_2Cl_2, which was dried over P_2O_5. Prepurified argon and hydrogen sulfide, obtained from Matheson, were used without further treatment. Carbon monoxide also was used as received. Hydrated rhodium(III) trichloride was obtained from Johnson Matthey Ltd., and $Re_2(CO)_{10}$ was purchased from Strem and sublimed before use. Benzenethiol and ethanethiol were obtained from Aldrich. All other chemicals were used as received without further purification. The 99% carbon-13-enriched carbon monoxide was obtained from Isotec Inc. The compound [RhRe(CO)$_4$(dppm)$_2$] (**1**) was prepared as previously reported.[8]

All NMR experiments were conducted on a Bruker AM-400 spectrometer operating at 161.9 MHz for ^{31}P. In all cases an internal deuterated solvent lock was used. In general, deuterated solvents were dried over P_2O_5, freeze–pump–thaw-degassed, and vacuum-distilled into the 5-mm NMR tube containing the sample. These tubes were flame-sealed with the contents at −196 °C for the variable-temperature NMR experiments.

Infrared spectra were recorded on either a Nicolet 7199 Fourier transform interferometer or a Perkin-Elmer 883 spectrophotometer, either as solids (Nujol mulls on KBr disks) or solutions (KCl cell windows, 0.5-mm path length). Spectral parameters for the compounds prepared are found in Table I. Elemental analyses were performed by the microanalytical service of our department.

Preparation of Compounds. (a) [RhRe(CO)$_4$(μ-S)(dppm)$_2$] (2). The compound [RhRe(CO)$_4$(dppm)$_2$] (**1**) (50 mg, 42.8 μmol) was dissolved in 5 mL of THF, and 2 mL of H_2S (~40 μmol/mL, 2 equiv) was added by gastight syringe. The solution slowly turned from yellow to dark orange-red over $^1/_2$ h. The solvent was then removed in vacuo to yield an orange residue, which was recrystallized from CH_2Cl_2/Et_2O to give 49 mg (95%) of an orange powder. Anal. Calcd for $C_{54}H_{44}O_4P_4ReRhS$: C, 53.96; H, 3.69; S, 2.67. Found: C, 53.62; H, 3.91; S, 2.95.

(b) [RhRe(CO)$_3$(μ-H)(μ-SEt)(dppm)$_2$] (5). Compound **1** (50 mg, 42.8 μmol) was dissolved in 5 mL of THF, and EtSH (3.2 μL, 42.9 μmol) was added by syringe. The yellow solution quickly turned dark orange-red and was stirred for $^1/_2$ h. Removal of the solvent in vacuo and recrystallization from CH_2Cl_2/Et_2O yielded 43 mg (84%) of an orange-red powder. Anal. Calcd for $C_{55}H_{50}O_3P_4ReRhS$: C, 54.80; H, 4.18. Found: C, 54.92; H, 4.33.

(c) [RhRe(CO)$_3$(μ-H)(μ-SPh)(dppm)$_2$] (6). Compound **1** (50 mg, 42.8 μmol) was dissolved in 5 mL of THF, and PhSH (4.4 μL, 42.9 μmol) was added by syringe. The solution immediately turned from yellow to dark red but was stirred for an additional $^1/_2$ h. Removal of the solvent in vacuo and recrystallization from CH_2Cl_2/Et_2O yielded 47 mg (89%) of an orange-red powder (**6**). Anal. Calcd for $C_{59}H_{50}O_3P_4ReRhS$: C, 56.60; H, 4.03. Found: C, 57.27; H, 4.29.

Low-Temperature NMR Studies. The solvent CD_2Cl_2 was vacuum-distilled into an NMR tube containing 50 mg (42.8 μmol) of compound **1** under argon at −196 °C. Benzenethiol, ethanethiol, or hydrogen sulfide was added by gastight syringe to the NMR tubes at −78 °C. These tubes were flame-sealed at −196 °C and then transferred to the NMR probe at −80 °C. The various NMR experiments were performed at this temperature, and then the probe was warmed in 10-deg intervals with the appropriate spectra being obtained at the different temperatures.

X-ray Data Collection. Red crystals of [RhRe(CO)$_3$(μ-H)(μ-SEt)(dppm)$_2$] (**5**) were obtained by slow evaporation of a concentrated solution of the complex in 1:1 THF/Et_2O. Several suitable crystals were mounted and flame-sealed under Ar in glass capillaries. Data were collected on an Enraf-Nonius CAD4 diffractometer with use of Mo Kα radiation. Unit-cell parameters were obtained from a least-squares refinement of the setting angles of 25 reflections in the range $20.0° \leq 2\theta \leq 24.0°$. A monoclinic crystal system was established by the usual peak search and reflection indexing programs, and systematic absences ($h0l$ (l = odd), $0k0$ (k = odd)) in the data were consistent with the space group $P2_1/c$.

Intensity data were collected at 22 °C by using the $\theta/2\theta$ scan technique to a maximum $2\theta = 50.0°$. Backgrounds were scanned for 25% of the peak width on either side of the peak. Three reflections were chosen as intensity standards and were remeasured at 120-min intervals of the X-ray exposure. There was no significant systematic decrease in the intensities of these standards, so no correction was applied. A total of 9654 unique reflections were measured and processed in the usual way using a value of 0.04 for p;[10] of these, 5011 were observed and were used in refinements.[11] Absorption corrections were applied to the data by

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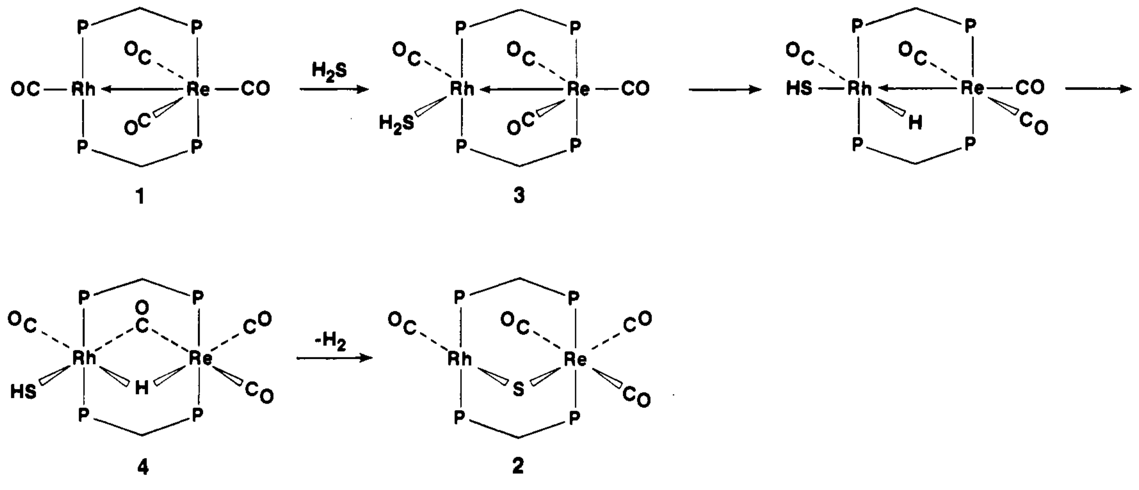
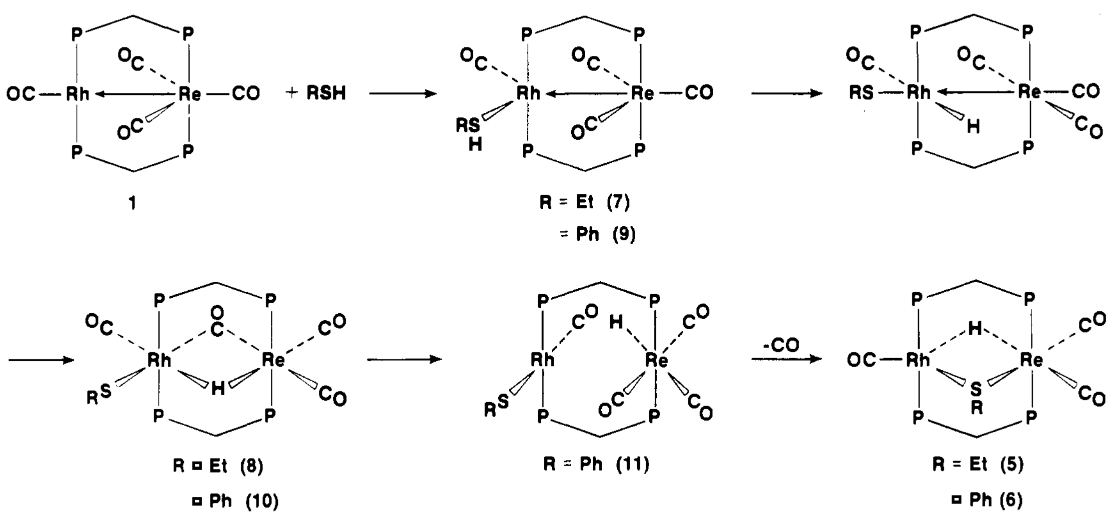
Scheme I



Scheme II



using the method of Walker and Stewart.[12]

Structure Solution and Refinement. The structure was solved in the space group $P2_1/c$ by using standard Patterson techniques to locate the Rh and Re atoms and the normal sequence of least-squares and difference Fourier cycles to locate all other atoms. Atomic scattering factors[13,14] and anomalous dispersion terms[15] were taken from the usual tabulations. All hydrogen atoms, with the exception of the hydride ligand, were included as fixed contributions but not refined. Their idealized positions were calculated from the geometries about the attached carbon atoms, and they were assigned thermal parameters 20% greater than the equivalent isotropic B's of their attached C atoms. One THF molecule was located, and apart from the large thermal parameters of this group, suggesting some disorder, it refined acceptably. The hydride ligand was successfully refined with use of an isotropic thermal parameter. The methyl group of the bridging ethanethiolate group did not behave well, suggesting that it was slightly disordered. Although the electron density associated with this carbon was diffuse, only one maximum was observed. The top 10 peaks in the final difference Fourier map (0.68–1.03 e/Å^3) were in the vicinities of the Re atom, the disordered methyl group of the thiolato ligand, and the THF molecule. A summary of the crystallographic data appears in Table II.

Results

The spectroscopic data for the compounds are collected in Table I, and the species characterized are shown in Schemes I and II.

Table II. Crystallographic Data for [RhRe(CO)$_3$(μ-H)(μ-SEt)(dppm)$_2$]·THF (5)

formula $C_{59}H_{58}O_4P_4SReRh$	space group: $P2_1/c$ (No. 14)
fw 1276.2	T = 22 °C
a = 12.216 (3) Å	λ = 0.71069 Å
b = 19.845 (7) Å	ρ_{calcd} = 1.540 g cm^{-3}
c = 23.316 (7) Å	μ = 27.175 cm^{-1}
β = 103.19 (2)°	transm coeff = 0.702–1.338
V = 5503 Å^3	$R(F_o)$ = 0.049
Z = 4	$R_w(F_o)$ = 0.056

The structure of compound **5** was determined by X-ray techniques; the positional and isotropic thermal parameters are given in Table III, and a description of the compound is given in the Discussion.

Discussion

The mixed-metal species [RhRe(CO)$_4$(dppm)$_2$] (**1**) reacts readily with 1 equiv of H$_2$S, yielding [RhRe(CO)$_4$(μ-S)(dppm)$_2$] (**2**) and H$_2$ quantitatively. This extremely facile reaction reconfirms the tendency of this low-valent species to undergo binuclear oxidative addition reactions[9] and also suggests that the coordinatively unsaturated Rh center is of paramount importance to the reactivity of this species. By comparison, the coordinatively saturated dirhenium analogue, [Re$_2$(CO)$_6$(dppm)$_2$], required rather vigorous conditions before reactions with substrates were observed,[16] owing to the necessity for prior CO loss.

Formulation of **2** is based on its elemental analyses and its spectroscopic data. Its IR spectrum displays four carbonyl stretches (see Table I) in a pattern very reminiscent of that observed (2046, 2001, 1937, 1908 cm^{-1}) for [RhRe(CO)$_4$(μ-H)-

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(11) Programs used were those of the Enraf-Nonius Structure Determination of Package by B. A. Frenz, in addition to local programs by R. G. Ball.

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Table III. Positional and Isotropic Thermal Parameters[a,b]

atom	*x*	*y*	*z*	*B*, Å[2c]
Re[c]	0.18442 (4)	0.11142 (2)	−0.22341 (2)	3.139 (8)
Rh	0.35985 (7)	0.21447 (5)	−0.17965 (4)	3.26 (2)
S	0.3912 (3)	0.0899 (2)	−0.1899 (2)	5.02 (8)
P(1)	0.2938 (2)	0.2333 (2)	−0.0968 (1)	3.46 (7)
P(2)	0.1472 (2)	0.1049 (2)	−0.1272 (1)	3.52 (6)
P(3)	0.3747 (2)	0.2457 (2)	−0.2725 (1)	3.40 (7)
P(4)	0.2203 (2)	0.1216 (2)	−0.3204 (1)	3.27 (6)
O(1)	0.5812 (7)	0.2771 (5)	−0.1239 (4)	6.6 (3)
O(2)	0.0655 (7)	−0.0230 (4)	−0.2551 (4)	7.0 (2)
O(3)	−0.0382 (7)	0.1830 (5)	−0.2682 (4)	7.1 (3)
C(1)	0.4979 (9)	0.2514 (6)	−0.1446 (5)	4.7 (3)
C(2)	0.113 (1)	0.0285 (6)	−0.2428 (5)	4.9 (3)
C(3)	0.0445 (9)	0.1538 (6)	−0.2503 (5)	4.3 (3)
C(4)	0.2369 (9)	0.1578 (5)	−0.0699 (5)	3.7 (3)
C(5)	0.3411 (8)	0.1760 (5)	−0.3263 (4)	3.3 (2)
C(6)	0.454 (1)	0.0566 (9)	−0.1174 (7)	9.6 (5)
C(7)	0.533 (2)	0.014 (2)	−0.108 (1)	26 (1)
C(11)	0.4007 (9)	0.2612 (6)	−0.0319 (5)	4.1 (3)*
C(12)	0.456 (1)	0.2187 (7)	0.0116 (6)	6.1 (3)*
C(13)	0.542 (1)	0.2447 (8)	0.0581 (6)	7.0 (4)*
C(14)	0.563 (1)	0.3099 (8)	0.0588 (6)	6.9 (4)*
C(15)	0.515 (1)	0.3539 (8)	0.0200 (6)	7.3 (4)*
C(16)	0.430 (1)	0.3295 (7)	−0.0278 (6)	6.0 (3)*
C(21)	0.1808 (8)	0.2938 (5)	−0.0987 (5)	3.5 (2)*
C(22)	0.1053 (9)	0.3072 (6)	−0.1522 (5)	4.6 (3)*
C(23)	0.015 (1)	0.3503 (8)	−0.1535 (6)	6.9 (4)*
C(24)	−0.000 (1)	0.3803 (7)	−0.1022 (6)	6.4 (3)*
C(25)	0.071 (1)	0.3662 (7)	−0.0501 (6)	6.5 (4)*
C(26)	0.161 (1)	0.3219 (6)	−0.0474 (5)	5.2 (3)*
C(31)	0.1622 (8)	0.0223 (6)	−0.0898 (5)	3.6 (2)*
C(32)	0.1299 (9)	0.0155 (6)	−0.0356 (5)	4.1 (2)*
C(33)	0.148 (1)	−0.0454 (6)	−0.0049 (5)	4.9 (3)*
C(34)	0.197 (1)	−0.0980 (7)	−0.0271 (6)	5.7 (3)*
C(35)	0.226 (1)	−0.0937 (8)	−0.0794 (6)	7.4 (4)*
C(36)	0.209 (1)	−0.0321 (7)	−0.1107 (6)	5.6 (3)*
C(41)	0.0018 (8)	0.1251 (5)	−0.1248 (5)	3.6 (2)*
C(42)	−0.0309 (9)	0.1801 (6)	−0.0971 (5)	4.5 (3)*
C(43)	−0.148 (1)	0.1934 (7)	−0.1025 (6)	5.6 (3)*
C(44)	−0.225 (1)	0.1514 (7)	−0.1331 (6)	5.6 (3)*
C(45)	−0.196 (1)	0.0955 (7)	−0.1598 (6)	6.1 (3)*
C(46)	−0.081 (1)	0.0823 (7)	−0.1560 (5)	5.4 (3)*
C(51)	0.5166 (8)	0.2680 (5)	−0.2790 (4)	3.4 (2)*
C(52)	0.548 (1)	0.3350 (7)	−0.2832 (5)	5.4 (3)*
C(53)	0.661 (1)	0.3495 (7)	−0.2858 (6)	6.2 (3)*
C(54)	0.735 (1)	0.2986 (8)	−0.2826 (6)	6.8 (4)*
C(55)	0.705 (1)	0.2325 (8)	−0.2792 (6)	7.0 (4)*
C(56)	0.596 (1)	0.2175 (7)	−0.2766 (5)	5.0 (3)*
C(61)	0.2866 (9)	0.3144 (6)	−0.3122 (5)	3.8 (2)*
C(62)	0.202 (1)	0.3391 (7)	−0.2903 (6)	6.0 (3)*
C(63)	0.127 (1)	0.3870 (8)	−0.3225 (6)	7.6 (4)*
C(64)	0.143 (1)	0.4060 (7)	−0.3766 (6)	6.8 (4)*
C(65)	0.228 (1)	0.3839 (7)	−0.3978 (5)	5.7 (3)*
C(66)	0.301 (1)	0.3373 (6)	−0.3658 (5)	4.9 (3)*
C(71)	0.2565 (9)	0.0465 (5)	−0.3579 (5)	3.8 (2)*
C(72)	0.281 (1)	−0.0145 (6)	−0.3297 (5)	4.9 (3)*
C(73)	0.309 (1)	−0.0721 (7)	−0.3577 (6)	5.7 (3)*
C(74)	0.308 (1)	−0.0684 (7)	−0.4168 (5)	5.4 (3)*
C(75)	0.286 (1)	−0.0076 (7)	−0.4469 (6)	6.0 (3)*
C(76)	0.261 (1)	0.0497 (7)	−0.4173 (6)	5.8 (3)*
C(81)	0.0959 (9)	0.1508 (5)	−0.3749 (5)	3.6 (2)*
C(82)	0.008 (1)	0.1051 (7)	−0.3897 (6)	6.1 (3)*
C(83)	−0.095 (1)	0.1271 (8)	−0.4278 (7)	7.5 (4)*
C(84)	−0.106 (1)	0.1921 (8)	−0.4490 (7)	7.3 (4)*
C(85)	−0.017 (1)	0.2355 (8)	−0.4368 (7)	7.6 (4)*
C(86)	0.085 (1)	0.2132 (7)	−0.3973 (6)	5.7 (3)*
H(1)	0.251 (9)	0.212 (6)	−0.216 (5)	5 (1)*

[a] Starred values indicate atoms were refined isotropically. [b] THF molecule values given in the supplementary material. [c] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

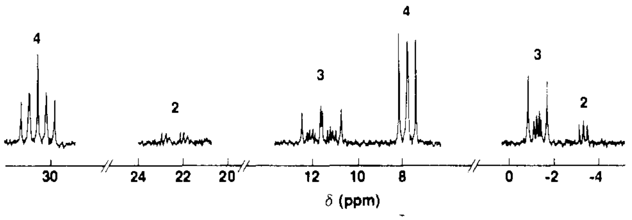
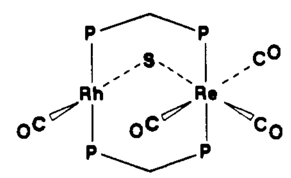


Figure 1. $^{31}P\{^1H\}$ NMR spectrum (at 161.9 MHz) at −60 °C for the reaction of $[RhRe(CO)_4(dppm)_2]$ with H_2S.

$(dppm)_2][BF_4]$, the structure of which has been determined.[9] The higher frequencies observed for the cationic species is consistent both with its positive charge and with the apparently excellent electron-donor capabilities of the bridging sulfide group in **1**; related sulfide-bridged complexes of Rh and Ir have also been observed to have low carbonyl stretches.[17-19] The $^{31}P\{^1H\}$ NMR spectrum of **2** displays a pattern consistent with an AA′BB′X spin system in which the diphosphine ligands bridge the metals in a trans arrangement, and the ^1H NMR spectrum shows no evidence of hydride species. The $^{13}C\{^1H\}$ NMR spectrum displays the expected four carbonyl resonances, with only the one at δ 193.5 showing obvious coupling to Rh ($^1J_{Rh-C}$ = 70 Hz). Consequently, structure **2** is proposed, in which the metals are bridged by the sulfide group, giving a square-planar configuration typical of a Rh(I) center, as observed in $[M_2(CO)_2(\mu\text{-}S)(dppm)_2]$ (M = Rh, Ir),[17,18] and giving a coordinatively saturated octahedral geometry for Re(I). However, when the $^{13}C\{^1H\}$ NMR spectrum is also broad-band ^{31}P-decoupled, the complex multiplet at low field (δ 215.8) resolves into an eight-line pattern in which coupling to two other carbonyl groups and to Rh becomes obvious ($^2J_{C-C}$ = 19 Hz, 4 Hz; $^1J_{Rh-C}$ = 9 Hz). This resonance corresponds to the carbonyl ligand on Re that is directed toward Rh; it displays a large coupling to the trans carbonyl and smaller coupling to the cis carbonyl group. The small value for the Rh coupling suggests that this ligand is best viewed as being terminally bound to Re, as shown, but having a weak semibridging interaction with Rh. The coupling between the other two Re-bound carbonyls ($^2J_{C-C}$ = 4 Hz) is also consistent with these groups being mutually cis. Oxidative addition of H_2S to the related binuclear species $[Pd_2Cl_2(dppm)_2]^3$ and $[Rh_2(CO)_3(dppm)_2]^2$ yielded rather analogous sulfide-bridged species, whereas the same reaction with $[Ir_2(CO)_3(dppm)_2]^2$ instead yielded a sulfide-bridged dihydride, which under more forcing conditions also yielded the sulfide-bridged analogue through H_2 loss.



2

In order to gain information about intermediates in the formation of **2**, which could then lead to a better understanding of how the two metals are involved, the above reaction was performed and monitored at low temperature by using ^1H, ^{13}C, and ^{31}P NMR spectroscopy. At −80 °C the $^{31}P\{^1H\}$ NMR spectrum shows only two species (**3** and **4**) in roughly equal proportions. Each species has a spectrum that is characteristic of an AA′BB′X spin system, displaying a second-order multiplet for the Re-bound phosphorus nuclei and a doublet of multiplets for those bound to Rh. Figure 1 shows the $^{31}P\{^1H\}$ spectrum at −60 °C, on which appears the resonances for **3** and **4** as well as those of the final product (**2**) (vide infra). The corresponding ^1H NMR spectrum (at −80 °C) shows two high-field resonances, at δ −0.85 (triplet) and −11.10 (multiplet), having chemical shifts that are characteristic of a sulfhydryl group[3,5-7,20,21] and a metal hydride, respectively.

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Heteronuclear phosphorus-decoupling experiments establish that both of these high-field resonances are associated with species **4** and also establish that the SH proton is coupled to the two phosphorus nuclei on Rh but displays no coupling to Rh, while the hydride ligand is coupled to Rh and to all four phosphorus nuclei. All resonances due to the dppm methylene groups can also be assigned on the basis of the decoupling experiments. The $^{13}C\{^1H\}$ NMR spectrum of a sample, which was 70% enriched with ^{13}CO, shows five carbonyl resonances. Four of these (three singlets and a doublet), belonging to **4**, integrate equally as one carbonyl each, while the fifth (a 280 Hz wide signal) integrates as four carbonyls, on the basis of the proportions of **3** and **4**, established by the $^{31}P\{^1H\}$ and ^1H NMR spectra. It appears, therefore, that both **3** and **4** are tetracarbonyl species and so are formulated as shown in Scheme I. Compound **3** is shown as an H_2S adduct even though no resonance can be established as due to a coordinated H_2S group. Assuming that this species is fluxional, as suggested by the $^{13}C\{^1H\}$ NMR spectrum, the H_2S may be rapidly exchanging with free H_2S in solution and may also be exchanging over both metals, as suggested by the one broad carbonyl resonance. This is assumed to occur by a "merry-go-round" exchange of the ligands (CO and H_2S) in the equatorial plane perpendicular to the metal–phosphine bonds, such that these ligands migrate around the $RhReP_4$ framework. In spite of our failure to observe a resonance for the coordinated H_2S group, we are confident of this formulation since the $^{31}P\{^1H\}$ NMR spectrum of the labile CO adduct of **1** has a very similar appearance to that of **3** and again displays only one broad carbonyl resonance.[9] Although this CO adduct also cannot be isolated, the isoelectronic species $[IrOs(CO)_5(dppm)_2][BF_4]$ has been structurally characterized[22] and shows the type of structure proposed for **3**.

Attempts to obtain a better model of the proposed H_2S adduct, **3** through addition of Me_2S to **1** were not successful since surprisingly no reaction was observed, even at −80 °C.

Transformation of **3** to **4** is envisioned as occurring via oxidative addition at Rh to give the intermediate shown, in which an octahedral Rh(III) center is formulated, and rearrangement to **4** should then be quite facile, explaining our failure to observe this precursor to **4**. Compound **4** is formulated as having a bridging carbonyl ligand, on the basis of the low-field resonance at δ 248 in the $^{13}C\{^1H\}$ NMR spectrum. However, this resonance displays no resolvable coupling to Rh, suggesting that its interaction with this metal is weak. Owing to the uncertainty involving the exact binding mode of this carbonyl ligand, it is difficult to make unambiguous assignments of the metal oxidation states and electron counts in this intermediate, although 18-electron configurations at both metals result if the bridging carbonyl donates one electron to each metal and if the bridged hydride is viewed as a Rh–H bond acting as a 2-electron donor to Re, as suggested later for compound **5** (vide infra). It should be noted that although the hydride-bridged species are drawn in the schemes without Rh–Re bonds, three-center Rh–H–Re interactions are implied.

Warming the solution to −60 °C leads to a substantial reduction in the concentration of **3**, as shown by the ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra, and a corresponding increase in the concentration of **4**. The final product **2** also appears at this temperature, as shown in Figure 1. No other species is observed over the temperature range between −80 and +20 °C, so clearly the presumed second oxidative addition step is followed by rapid reductive elimination of H_2.

In an attempt to obtain further information about the monohydride intermediates in this binuclear oxidative addition reaction, we attempted to model the H_2S chemistry by following the analogous reactions with thiols. Although compound **1** also reacts readily with the thiols HSEt and HSPh by oxidative addition of the H–S bond, as was the case for H_2S, the final products are not totally analogous to any of the proposed intermediates in the H_2S reaction. In particular, the reactions with these thiols result in CO loss to yield the tricarbonyl complexes $[RhRe(CO)_3(\mu\text{-}H)(\mu\text{-}SR)(dppm)_2]$ (R = Et (**5**), Ph (**6**)). Both species display three carbonyl bands in the IR spectra and also have $^{31}P\{^1H\}$ spectra as expected for an AA′BB′X spin system. The ^1H NMR spectrum displays a high-field multiplet for each species, at δ −10.5 (**5**) and −9.7 (**6**), and selective ^{31}P decoupling experiments clearly indicate that the hydride ligand in each compound bridges the metals, displaying coupling to Rh and to all phosphorus nuclei (see Table I).

The X-ray structure determination of **5** confirms our formulation and furthermore establishes that the thiolato group bridges the metals on the *opposite* face of the dimer from the hydride ligand. Although this may appear to be unusual, facile tunneling of a hydride ligand from one face of a dimer to the other has been previously proposed[19,23] in similar systems. Figure 2 shows a

Table IV. Bond Lenghts (Å) for $[RhRe(CO)_3(\mu\text{-}H)(\mu\text{-}SEt)(dppm)_2]$[a]

Re–Rh	2.9697 (8)	P(1)–C(21)	1.823 (9)
Re–S	2.505 (3)	P(2)–C(4)	1.850 (9)
Re–P(2)	2.392 (2)	P(2)–C(31)	1.846 (9)
Re–P(4)	2.408 (2)	P(2)–C(41)	1.834 (9)
Re–C(2)	1.87 (1)	P(3)–C(5)	1.849 (9)
Re–C(3)	1.88 (1)	P(3)–C(51)	1.828 (9)
Re–H(1)	2.1 (1)	P(3)–C(61)	1.84 (1)
Rh–S	2.521 (3)	P(4)–C(5)	1.858 (9)
Rh–P(1)	2.287 (3)	P(4)–C(71)	1.831 (9)
Rh–P(3)	2.299 (3)	P(4)–C(81)	1.839 (9)
Rh–C(1)	1.85 (1)	O(1)–C(1)	1.14 (1)
Rh–H(1)	1.4 (1)	O(2)–C(2)	1.18 (1)
S–C(6)	1.81 (1)	O(3)–C(3)	1.16 (1)
P(1)–C(4)	1.821 (9)	C(6)–C(7)	1.27 (2)
P(1)–C(11)	1.84 (1)		

[a] Bond lengths for the phenyl rings and the THF molecule are given in the supplementary material.

Table V. Selected Angles (deg) for $[RhRe(CO)_3(\mu\text{-}H)(\mu\text{-}SEt)(dppm)_2]$[a]

Rh–Re–S	54.04 (6)	C(1)–Rh–H(1)	158 (4)
Rh–Re–P(2)	89.53 (6)	Re–S–Rh	72.44 (8)
Rh–Re–P(4)	89.62 (6)	Re–S–C(6)	122.3 (5)
Rh–Re–C(2)	161.9 (3)	Rh–S–C(6)	108.1 (5)
Rh–Re–C(3)	109.6 (3)	Rh–P(1)–C(4)	113.1 (3)
Rh–Re–H(1)	26 (3)	Rh–P(1)–C(11)	114.9 (3)
S–Re–P(2)	95.28 (9)	Rh–P(1)–C(21)	119.9 (3)
S–Re–P(4)	85.45 (9)	C(4)–P(1)–C(11)	102.7 (4)
S–Re–C(2)	108.0 (3)	C(4)–P(1)–C(21)	101.7 (4)
S–Re–C(3)	162.9 (3)	C(11)–P(1)–C(21)	102.2 (4)
S–Re–H(1)	78 (3)	Re–P(2)–C(4)	116.0 (3)
P(2)–Re–P(4)	178.25 (9)	Re–P(2)–C(31)	118.1 (3)
P(2)–Re–C(2)	90.1 (3)	Re–P(2)–C(41)	114.2 (3)
P(2)–Re–C(3)	89.1 (3)	C(4)–P(2)–C(31)	100.6 (4)
P(2)–Re–H(1)	97 (3)	C(4)–P(2)–C(41)	105.8 (4)
P(4)–Re–C(2)	91.2 (3)	C(31)–P(2)–C(41)	99.9 (4)
P(4)–Re–C(3)	89.8 (3)	Rh–P(3)–C(5)	112.6 (3)
P(4)–Re–H(1)	81 (3)	Rh–P(3)–C(51)	115.0 (3)
C(2)–Re–C(3)	88.5 (5)	Rh–P(3)–C(61)	121.0 (3)
C(2)–Re–H(1)	170 (2)	C(5)–P(3)–C(51)	101.2 (4)
C(3)–Re–H(1)	85 (3)	C(5)–P(3)–C(61)	101.6 (4)
Re–Rh–S	53.52 (7)	C(51)–P(3)–C(61)	102.9 (4)
Re–Rh–P(1)	92.10 (7)	Re–P(4)–C(5)	115.9 (3)
Re–Rh–P(3)	93.87 (7)	Re–P(4)–C(71)	119.7 (3)
Re–Rh–C(1)	159.8 (3)	Re–P(4)–C(81)	112.1 (3)
Re–Rh–H(1)	42 (4)	C(5)–P(4)–C(71)	98.9 (4)
S–Rh–P(1)	109.3 (1)	C(5)–P(4)–C(81)	108.1 (4)
S–Rh–P(3)	97.4 (1)	C(71)–P(4)–C(81)	100.3 (4)
S–Rh–C(1)	106.7 (3)	Rh–C(1)–O(1)	177 (1)
S–Rh–H(1)	93 (4)	Re–C(2)–O(2)	179 (1)
P(1)–Rh–P(3)	150.5 (1)	Re–C(3)–O(3)	175.8 (9)
P(1)–Rh–C(1)	91.4 (3)	P(1)–C(4)–P(2)	115.4 (5)
P(1)–Rh–H(1)	93 (4)	P(3)–C(5)–P(4)	116.2 (4)
P(3)–Rh–C(1)	92.9 (3)	S–C(6)–C(7)	123 (2)
P(3)–Rh–H(1)	73 (4)	Re–H(1)–Rh	112 (5)

[a] Angles for the phenyl rings and the THF molecule are given in the supplementary material.

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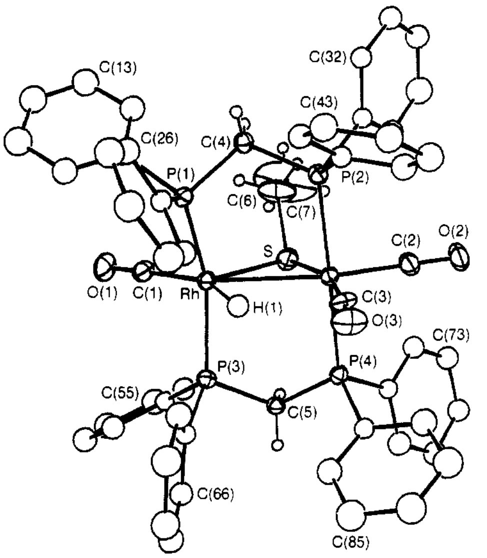
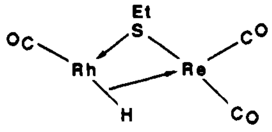


Figure 2. Perspective view of $[RhRe(CO)_3(\mu\text{-}H)(\mu\text{-}SEt)(dppm)_2]$ (**5**) showing the numbering scheme. Thermal parameters are shown at the 20% level except for the methylene hydrogens on the dppm ligands and the hydrogens on the ethanethiolate group, which are drawn arbitrarily small. Phenyl hydrogens are omitted.

perspective view of compound **5**, and relevant bond lengths and angles are given in Tables IV and V. If the Rh–Re interaction is ignored, the geometry about Rh is that of a tetragonal pyramid in which S occupies the apical site and P(1), P(3), C(1), and H(1) occupy the basal sites. The P(1)–Rh–P(3) and C(1)–Rh–H(1) angles of 150.5 (1) and 158 (4)°, respectively, and the angles between S and the four basal groups of between 93 (4) and 109.3 (1)° are consistent with this description. About Re the geometry is a distorted octahedron in which H(1) or, more appropriately, the Rh–H(1) bond can be considered as occupying the sixth site opposite C(2) (vide infra). The major distortions result from the strain imposed by the bridging thiolate group and the associated acute Rh–S–Re angle of 72.44 (8)°. Consistent with the distorted octahedral geometry about Re, the P(2)–Re–P(4) angle (178.25 (9)°) is close to linear, unlike the analogous phosphine arrangement about Rh, and all other angles, apart from those involving sulfur but including those involving H(1), are near the idealized values. The Re–P distances (2.392 (2), 2.408 (2) Å) are longer than the Rh–P distances (2.287 (3), 2.299 (3) Å), consistent with the larger covalent radius of Re compared to Rh.[24] All other parameters within the diphosphine and carbonyl groups are as expected.

The unusual aspects of the structure involve the central core of the metals and the hydride and thiolate ligands. We suggest that the parameters involving these groups imply a bonding pattern as shown in **5**. In spite of the larger metallic radius of Re, the



5

Re–S distance (2.505 (3) Å) is *shorter* than the Rh–S distance (2.521 (3) Å) and suggests that the thiolate ligand functions as an anionic group toward Re, binding to Rh via a weaker dative bond. The Rh–S interaction appears to be substantially weaker than the comparable interactions in the sulfhydryl-bridged species $[RhCl(H)(\mu\text{-}SH)(PPh_3)_2]_2$[4] and the sulfide-bridged species $[Rh_2(CO)_2(\mu\text{-}S)(dppm)_2]$,[17] in which Rh–S distances of 2.384 (1) and 2.367 (3) Å, respectively, were observed, lending support to our proposal of a weaker dative interaction in **5**. The sixth coordination site on Re (opposite C(2)) is then occupied by the Rh–H bond, which forms an agostic-like interaction with Re. This three-center Rh–H–Re interaction would be expected to result in a longer Rh–Re distance than in a two-electron, two-center interaction between the metals; consequently, the Rh–Re distance (2.9697 (8) Å) in **5** is much longer than in the precursor **1** (2.7919 (6) Å).[8] Such a view of bridged hydrides has been considered previously[25] and can be a useful way of considering the three-centered two-electron M–H–M′ interaction. Also consistent with such a description, the Rh–H(1) bond (1.4 (1) Å) is substantially shorter than the Re–H(1) distance (2.1 (1) Å), although in reality these distances are not accurately determined owing to the dominant X-ray scattering by the heavy metals. Therefore, the true hydride location is probably further from Rh and closer to Re by as much as 0.2–0.3 Å.

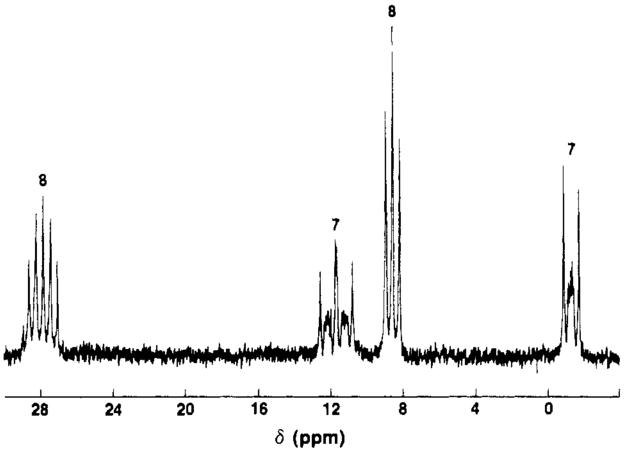


Figure 3. $^{31}P\{^1H\}$ NMR spectrum at −80 °C for the reaction of $[RhRe(CO)_4(dppm)_2]$ with HSEt.

The geometry within the bridging thiolato group is normal, although there is clearly disorder of the methyl carbon about several closely spaced, unresolved positions.

In an attempt to again characterize intermediates in these transformations involving the thiols, we monitored these reactions by NMR spectroscopy at low temperatures. In the reaction of **1** with HSEt at −80 °C, only two products are again observed in the $^{31}P\{^1H\}$ spectrum, as shown in Figure 3. It is significant that even at −80 °C there is no evidence of starting material, indicating that **1** is clearly reactive. The two intermediates observed (**7** and **8**) have $^{31}P\{^1H\}$ NMR patterns almost superimposable on those observed in the H_2S reaction and so are given analogous formulations, as shown in Scheme II. Compound **7** is proposed to be an EtSH adduct, although again we failed to detect the ^1H NMR signal for the coordinated thiol. Species **8** contains a hydrido ligand, which bridges both metals, as shown by the hydride resonance at δ −11.1, displaying coupling to Rh and the four phosphorus nuclei. The $^{13}C\{^1H\}$ NMR spectrum shows that both species are tetracarbonyls, and again the first adduct (**7**) displays only a broad resonance integrating as four carbonyl groups, while **8** shows four separate resonances integrating as one carbonyl each. The presence of only one broad carbonyl resonance in the $^{13}C\{^1H\}$ NMR spectrum of **7** again suggests a process that exchanges all carbonyls, possibly via a "merry-go-round" process as suggested for compound **3**. Significantly, in a related reaction of a Pt_3 cluster with thiols, a fluxional HSR adduct was proposed and again no resonance due to the thiol was observed.[26] Monitoring this reaction as the temperature is increased shows a decrease in all NMR resonances due to **7** with a concomitant increase in those of **8**. Resonances due to **5** do not appear until approximately −20 °C, and by ambient temperature only this species remains. No additional res-

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onances appear throughout the temperature range investigated.

The reaction involving benzenethiol proceeds in much the same manner except that an additional species (**11**) appears at -80 °C, together with **9** and **10**, which appear exactly analogous to **7** and **8**, respectively. Compound **11** displays a hydride resonance, a broad singlet at δ -10.65, in the ^{1}H NMR spectrum, and selective ^{31}P decoupling shows that it is bound only to Re, since no effect is observed on irradiating the Rh-bound phosphorus nuclei, whereas collapse to a narrower signal is observed when the Re-bound phosphorus nuclei are decoupled. The $^{13}C\{^{1}H\}$ NMR spectrum also shows that this intermediate is a tetracarbonyl. We therefore propose the structure shown in Scheme II for **11**. Although we cannot unambiguously establish whether the thiolato group and the hydride ligand are on opposite faces of the dimer, as shown, this appears reasonable on the basis of the structure determination of **5**.

It is apparent that the initial stages in the reactions of **1** with H_2S and thiols are analogous. We first observe the simple HSR (R = H, Et, Ph) adducts, in which these groups presumably coordinate at the unsaturated Rh center, followed by oxidative addition to yield a bridging hydride species. Not unexpectedly, the pathways involving H_2S and the thiols begin to diverge after this, since for H_2S, oxidative addition of the second H-S linkage can occur, whereas the analogous process is much less facile for the R-S linkage of the thiolato group. An intermediate such as **11**, which was only observed for HSPh, may also be important in the second oxidative addition of H_2S, since, as formulated, this yields a coordinatively unsaturated Rh(I) center that can then oxidatively add to the coordinated S-H moiety, giving a dihydride species which then reductively eliminates H_2 very readily. In the case of the thiols, for which the second oxidative addition reaction does not occur, another pathway, in which the terminal thiolato group on Rh forms a dative bond to Re with expulsion of CO, becomes favorable.

Throughout these studies we find no evidence that the Re atom is directly involved in the oxidative addition reactions. However it is clear that this atom plays a significant role. It appears that Re can serve to generate coordinative unsaturation at Rh after the first oxidative addition step, both by cleavage of the Re→Rh dative bond and possibly by accepting a hydrido ligand, as shown in the HSPh reaction (species **11**). By contrast, the mononuclear complexes $[RhCl(PPh_3)_3]$ and $[IrCl(CO)(PPh_3)_2]$ were also found to undergo the first oxidative addition step with H_2S,[4] but in neither case did oxidative addition of the second S-H bond occur, presumably since the products of the first oxidative additions were in the +3 oxidation states and were much less prone to further oxidative addition. Subsequent reaction of compound **4**, via transfer of the hydride ligand to Re yielding a species analogous to **11**, is akin to reductively eliminating the "$HRe(CO)_3P_2$" moiety to regenerate a Rh(I) center, which is again capable of oxidatively adding to the second S-H bond. The structure determination of **5** also lends support to the idea that facile electron and ligand reorganization over the central core can occur. Although the thiolato group in intermediate **11** is apparently bound to Rh with the hydride on Re, the reverse appears more appropriate in **5**, with the hydride ligand more closely associated with Rh and the thiolate more tightly bound to Re. Such reorganization is clearly important in promoting reactivity in these mixed-metal systems.

Currently we are attempting to obtain additional information on the intermediates in such reactions with aims of learning more about the involvement of the Re center in this chemistry.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada (NSERC) and the University of Alberta for financial support and NSERC for partial support for the purchase of the diffractometer and for funding of the PE883 IR spectrometer.

Supplementary Material Available: Tables giving anisotropic thermal parameters, additional bond lengths and angles, hydrogen atom parameters, a summary of crystallographic data, and positional parameters for all atoms (9 pages); listings of the observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

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Syntheses of Monomeric (η^5-Pentamethylcyclopentadienyl)platinum(IV) Methyl and Bromo Complexes and of [Hydrotris(3,5-dimethyl-1-pyrazolyl)borato]trimethylplatinum

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Received January 24, 1990

The reaction of $Cp^*MgCl\cdot THF$ ($Cp^* = C_5Me_5$) with 1 equiv of $PtMe_3I$ and $PtMe_2Br_2$ produces Cp^*PtMe_3 (**1**) and Cp^*PtMe_2Br (**2**), respectively. Reaction of **2** with Br_2 produces $Cp^*PtMeBr_2$ (**3**) in good yield. The structures of **2** and **3** have been determined by X-ray crystallography. Complex **2** crystallizes in the monoclinic space group, $P2_1/m$, with a = 7.017 (4) Å, b = 11.573 (4) Å, c = 8.496 (3) Å, β = 98.59 (3)°, Z = 2, V = 682.1 Å^3, R = 0.067, and R_w = 0.081. Complex **3** also crystallizes in the monoclinic space group, $P2_1/m$, with a = 7.147 (2) Å, b = 12.171 (4) Å, c = 8.617 (2) Å, β = 113.77 (2)°, Z = 2, V = 685.9 Å^3, R = 0.036, and R_w = 0.053. The molecules reside on mirror planes and are monomeric pseudotetrahedral Pt(IV) complexes with "piano stool" type geometries and η^5-Cp^* groups. Both molecules have Br atoms on the mirror. This leads to a disorder of the Me and the second Br positions in complex **3**. The average Pt-C(Cp^*) bond length is 2.25 (7) Å in **2** and 2.22 (4) Å in **3**. The Pt-C(Me) and Pt-Br bond lengths in **2** are 2.07 (2) and 2.498 (2) Å, respectively. The ordered Pt-Br bond length in **3** is 2.496 (2) Å. Treatment of **1** with halogens results in the cleavage of the Pt-Cp^* bond. The reaction of $PtMe_3I$ with KTp^* ($Tp^* = [HB\text{-}(3,5\text{-dimethylpyrazolyl})_3]^-$) in thf gives Tp^*PtMe_3 (**4**) in almost quantitative yield. The reaction of **4** with Br_2 brominates the 4-position of the pyrazolyl ring only.

Introduction

While the organometallic chemistry of the group VIII metals Rh and Ir with the Cp^* ($Cp^* = C_5Me_5$) ligand has rapidly developed over the past 10–15 years, that of analogous Pt systems has progressed little.[1-4] A major obstacle to development of the Pt systems is the absence of the Pt analogue of $[Cp^*MCl_2]_2$ (M = Rh, Ir), the major starting material for the Rh and Ir systems. Although a Cp^* bromo complex of Pt(IV) has been reported, it is obtained in poor yield and is poorly characterized.[5] In this

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