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Rhodium hydride complexes with phosphite / phosphito ligands: syntheses, reactions with isocyanates and the X-ray crystal structure of $HRh\{[P(OMe)_2O]_2H\}_2(PPh_2Me)$

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Abstract

The recently reported complex, $HRh\{[P(OMe)_2O]_2H\}_2(CO)$, is of interest because it contains both a metal hydride and an acidic proton. The carbonyl ligand in this complex is readily displaced by P-donor ligands. The bridging protons in the phosphite/phosphito ligands can be replaced by BF_2 groups. These complexes do not react with carbon dioxide or carbon disulfide at room temperature and pressure, but the carbonyl complexes react with isocyanates to yield ureas and oligomers of the isocyanates. The major P-containing compound isolated from these reactions is $[Rh\{[P(OMe)_2O]_2H\}_3]$. The reaction of $HRh\{[P(OMe)_2O]_2BF_2\}_2(CO)$ with isocyanates gives a complex mixture of P-containing products in which cleavage of the P–O–B bond has occurred.

The X-ray crystal structure of $HRh\{[P(OMe)_2O]_2H\}_2(PPh_2Me)$ is also reported. The complex crystallizes in the orthorhombic space group $Pna2_1$ (a 19.523(1), b 13.510(1), c 12.353(3) Å, V 3259.1 Å^3, $Z = 4$). The complex exhibits a distorted octahedral structure with the Rh displaced out of the plane of the phosphite/ phosphito ligands towards the PPh_2Me ligand. The two phosphite/phosphito chelate rings in this complex are quite different with one planar and the other significantly distorted from a plane. This appears to be due to the different orientations of the phenyl groups of the PPh_2Me ligand.

Introduction

A variety of transition metal complexes in which mutually cis-coordinated PR_2O^- and PR_2OH ligands form a hydrogen-bonded ring, as shown below, have been synthesized. These complexes can be obtained by the addition of phosphinous acids or their salts to suitable metal complexes [1–5], by the hydrolysis of

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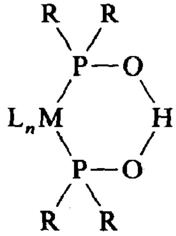
halophosphines [6–8], phosphinites or phosphites [1,9–12], alkynylphosphines [13] or cyanophosphines [14] or by the oxidation of phosphido ligands [15].



These ligands are of interest for several reasons. One is that the chelate rings in these ligands exhibit unusually small O–O distances [1–4,9,11,15,16]. This suggests that the H may be strongly bound to both O's. A second is that the bridging proton can be replaced with a variety of other groups to form unusual chelate rings [1,6,17–22]. The chelate rings in these complexes exhibit a variety of conformations depending upon the P substituents and the bridging group. Perhaps the most important is that the ligands contain both soft (P) and hard (O) donor sites and can be used to form heterometallic complexes containing both hard and soft metals [1,23,34]. The two metal ions, thus held in close proximity, may provide a geometry suitable for the catalysis of reactions that cannot be catalyzed with mononuclear complexes.

Complexes of the type $HM\{[P(R)_2O]_2H\}_2L$ ($L = CO$, $HOP(OR)_2$; $R_2 = (OMe)_2$, $(OEt)_2$, $OCH_2CMe_2CH_2O$; $M = Rh$, Ir) have recently been reported [4,5]. These complexes are of interest because they contain both a metal hydride and an acidic bridging proton. These are held in a configuration that may be suitable for the bifunctional activation of carbon dioxide and other heteroallenes. We have initiated a study of the reactions of $HRh\{[P(OMe)_2O]_2H\}_2(CO)$, with a variety of phosphines and heteroallenes. We report here the results of these studies and the X-ray crystal structure of $HRh\{[P(OMe)_2O]_2H\}_2(PPh_2Me)$.

Experimental

All reactions were carried out under a dry N_2 atmosphere. Both tetrahydrofuran (THF) and diethyl ether were distilled from Na-benzophenone. Other solvents were used as received. Literature methods were used to prepare $[Et_4N][cis\text{-}Mo(CO)_4(PPh_2O)_2H]$ [6], $[Et_4N][cis\text{-}Mo(CO)_4(PPh_2OHSPPh_2)]$ [35] and (acac)-$Rh(CO)_2$ [36].

Multinuclear NMR spectra of 0.10 *M* chloroform-d_1 solutions of all complexes were run on a GE NT-300 wide bore multinuclear NMR spectrometer. Proton NMR spectra of chloroform-d_1 solutions of the ligands were taken on a Varian 360L NMR spectrometer. Infrared spectra of KBr disks of the complexes were run on a Perkin Elmer 283B IR or a Nicolet IR 42 FT-IR spectrometer. The spectroscopic data are summarized in Tables 1 and 2.

$HRh\{[P(OMe)_2O]_2H\}_2(CO)$ (I)

Neat dimethyl phosphite (1 ml) was added dropwise to a stirred solution of 0.44 g (1.71 mmol) of (acac)$Rh(CO)_2$ in 30 ml of hexanes at 50 °C. During the addition, the solution remained clear, and its color changed from pale yellow to light brown and then finally to pale yellow. When the addition was completed, the solution was stirred at 50 °C for 30 min and then cooled at −5 °C. After several hours 0.85 g (90%) of white, analytically pure I (decomposed above 270 °C) was collected by filtration. Anal. Found: C, 18.81; H, 4.77. $C_9H_{27}O_{13}P_4Rh$ calc.: C, 18.95; H, 4.73%.

$HRh\{[P(OMe)_2O]_2H\}_2(PPh_2Me)$ (II)

A solution of 0.15 g (0.26 mmol) of I and 0.053 g (0.26 mmol) of diphenylmethylphosphine in 5 ml $CDCl_3$ was stirred at ambient temperature, and the course of the reaction was followed by ^1H NMR spectroscopy. When the reaction was completed (20 h), the reaction mixture was evaporated to dryness to yield 0.21 g (100%) of crude II as a pale-yellow solid. Recrystallization from pure hexanes gave analytically pure II (decomposed above 150 °C). Anal. Found: C, 34.04; H, 5.45. $C_{21}H_{40}O_{12}P_5Rh$ calc.: C, 33.97; H, 5.39%.

$HRh\{[P(OMe)_2O]_2H\}_2(P^nBu_3)$ (III)

A solution of 0.11 g (0.53 mmol) of tri-n-butylphosphine and 0.30 g (0.53 mmol) of I in 10 ml of diethyl ether was stirred at ambient temperature overnight. The solution was then evaporated to dryness to give 0.33 g (84%) of crude III as a pale yellow solid. Recrystallization from hexanes yielded analytically pure III (m.p. 123–125 °C). Anal. Found: C, 32.49; H, 7.41. $C_{20}H_{54}O_{12}P_5Rh$ calc.: C, 32.26; H, 7.26%.

$HRh\{[P(OMe)_2O]_2H\}_2\{P(O^iPr)_3\}$ (IV)

A solution of 0.20 g (0.35 mmol) of I and 0.073 g (0.35 mmol) of triisopropyl phosphite in 5 ml of ether was stirred for 4 d at ambient temperature. The cloudy solution was then filtered through diatomaceous earth, and the filtrate was evaporated to dryness to yield 0.27 g (100%) of crude IV. Decomposition of the product occurred during attempted recrystallization from hexanes.

$HRh\{[P(OMe)_2O]_2BF_2\}_2(CO)$ (V)

A solution of 0.11 g (0.19 mmol) of I and 0.30 ml of boron trifluoride diethyl etherate in 10 ml of diethyl ether was stirred at ambient temperature overnight. The solution was then evaporated to dryness, and the residue was washed with diethyl ether to yield 0.12 g (92%) of analytically pure $V \cdot 1/8Et_2O$ as a white powder (decomposes above 200 °C). Anal. Found: C, 16.84; H, 3.70. $C_9H_{25}B_2F_4O_{13}P_4Rh \cdot 1/8Et_2O$ calc.: C, 16.89; H, 3.89%.

$HRh\{[P(OMe)_2O]_2BF_2\}_2(PMePh_2)$ (VI)

Using the method described for the preparation of V, 0.20 g (0.27 mmol) of II and 0.75 ml of boron trifluoride diethyl etherate yielded 0.18 g (80%) of VI as a sticky white solid. Because VI did not completely solidify after the diethyl ether wash, it was characterized by NMR spectroscopy and was not submitted for elemental analyses.

$HRh\{[P(OMe)_2O]_2BF_2\}_2(P^nBu_3)$ (VII)

Using the method described for the preparation of V, 0.12 g (0.16 mmol) of III and 0.45 ml of boron trifluoride diethyl etherate yielded 0.12 g (90%) of analytically

Table I

^{31}P NMR data for the HRh{[P(OMe)$_2$O]$_2$X}$_2$L complexes [a]

Compound	X	L [b]	Phosphite		P′			P″		
			δ ^{31}P (ppm)	^1J(RhP) (Hz)	δ ^{31}P (ppm)	^1J(RhP′) (Hz)	^2J(PP′) (Hz)	δ ^{31}P (ppm)	^nJ(P′P″) (Hz)	n
I	H	CO	105.60 d	121						
II	H	P′Ph$_2$Me	112.06 dd	126	3.60 dq	81	33			
III	H	P′^{n}Bu$_3$	113.62 dd	127	−5.65 dq	80	33			
IV	H	P′(O^{i}Pr)$_3$	112.02 dd	127	120.47 dq	126	44			
V	BF$_2$	CO	101.52 d	125						
VI	BF$_2$	P′Ph$_2$Me	104.67 dd	131	0.55 dq	81	32			
VII	BF$_2$	P′^{n}Bu$_3$	106.63 dd	131	−6.35 dq	79	33			
VIII	H	Ph$_2$P′CH$_2$P″(O)Ph$_2$	111.48 dd	127	12.50 m	–	32	26.23 d	32	2
IX	H	1/2 Ph$_2$P′(CH$_2$)$_2$P′Ph$_2$	111.72 dd	127	17.30 m	–	32			
X	H	Ph$_2$P′(CH$_2$)$_2$P″Ph$_2$	111.78 dd	127	16.80 m	–	32	−12.71 d	32	3
XI	H	Ph$_2$P′(CH$_2$)$_2$P″(O)Ph$_2$	111.45 dd	126	16.80 m	–	32	32.62 d	34	3

[a] d = doublet, dd = doublet of doublets, dq = doublet of quintets, m = multiplet. [b] P′ is always coordinated to Rh, P″ is either free (X) or oxidized (VIII and XI).

Table 2

Other spectroscopic data for the $HRh\{[P(OMe)_2O]_2X\}_2L$ complexes. [a]

Compound	X	L	^{13}C NMR		^{1}H NMR				IR	
			δ ($POCH_3$) (ppm)	^2J(PC) (Hz)	δ (RhH) (ppm)	^1J(RhH) (Hz)	^2J(PH) (Hz)	^2J(P'H) (Hz)	ν(CO) (cm^{-1})	ν(RhH) (cm^{-1})
I	H	CO	50.74 d	10.	−9.40 dq	14	9		2103 s	2005 m
II	H	$P'Ph_2Me$	50.35 d	33	−10.16 ddq	18	12	140.	–	1995 m
III	H	P'^nBu_3	50.23 d	27	−10.16 ddq	12	12	135	–	1998 m
IV	H	$P'(O^iPr)_3$	50.42 d	18	[b]				–	1992 m
V	BF_2	CO	52.56 d	10.	[b]				2124 s	2013 m
VI	BF_2	$P'Ph_2Me$	51.99 d	11	[b]				–	2008 m
VII	BF_2	P'^nBu_3	51.90 d	15	[b]				–	2003 m

[a] d = doublet, dq = doublet of quintets, ddq = doublet of doublet of quintets, s = strong, m = medium. [b] The observation of the hydride resonance was difficult and required relatively large amounts of sample. These complexes were not prepared in sufficiently large quantities for this resonance to be observed.

pure VII as a white powder (m.p. 187–189 °C). Anal. Found: C, 28.68; H, 6.19. $C_{20}H_{52}B_2F_4O_{12}P_5Rh$ calc: C, 28.68; H, 6.27%.

Reaction of HRh{[P(OMe)$_2$O]$_2$H}$_2$(CO) with dppm

A solution of 0.50 g (0.88 mmol) of I and 0.17 g (0.44 mmol) of bis(diphenylphosphino)methane (dppm) was stirred in 10 ml diethyl ether for 18 h. The reaction mixture was then evaporated to dryness, and a ^{31}P NMR spectrum of the residue was recorded. The residue appeared to contain mostly unreacted I as well as small amounts of $Ph_2P(O)CH_2P(O)Ph_2$ (^{31}P NMR: δ 22.46 (s)) and $HRh\{[P(OMe)_2O]_2H\}_2\}_2(Ph_2PCH_2P(O)Ph_2)$ (VIII). Longer reaction times and attempts to separate these components by fractional recrystallization resulted in the decomposition of the material.

Reaction of HRh{[P(OMe)$_2$O]$_2$H}$_2$(CO) with dppe

A solution of 0.50 g (0.88 mmol) of I and 0.35 g (0.88 mmol) of bis(diphenylphosphino)ethane (dppe) in 30 ml of diethyl ether was stirred at ambient temperature for 24 h during which time a yellow solid precipitated from the solution. This material was collected by filtration (0.17 g) and dissolved in methanol. The methanol solution was filtered and evaporated to dryness to give a yellow residue. The ^{31}P NMR spectrum of the residue indicated that it contained primarily $[HRh\{[P(OMe)_2O]_2H\}_2]_2(\mu\text{-}Ph_2PCH_2CH_2PPh_2)$ (IX), and a small amount of $Ph_2P(O)CH_2CH_2P(O)Ph_2$ (^{31}P NMR: δ 33.55 ppm (s)). The filtrate of the reaction mixture was evaporated to dryness to yield 0.58 g of a yellow residue. A ^{31}P NMR spectrum of this residue indicated that it contained approximately equal amounts of $HRh\{[P(OMe)_2O]_2H\}_2(Ph_2PCH_2CH_2PPh_2)$ (X), and $HRh\{[P(OMe)_2O]_2H\}_2(Ph_2PCH_2CH_2P(O)Ph_2$ (XI), and small amounts of IX and $Ph_2P(O)CH_2CH_2P(O)Ph_2$. The residue was then dissolved in dichloromethane and O_2 was bubbled into the solution for 5 d, before the reaction mixture was evaporated to dryness. A ^{31}P NMR spectrum of the residue indicated that X was completely oxidized to XI during this time. Attempts to separate both IX and XI from the $Ph_2P(O)CH_2CH_2P(O)Ph_2$ by fractional crystallization were not successful, and analytically pure products could not be obtained.

Rh[P(OMe)$_2$O]$_3$ (XII)

A solution of 0.10 g (0.18 mmol) of I in wet THF was stirred at ambient temperature for 9 d. The mixture was then filtered to yield 0.03 g (40%) of analytically pure XII (m.p. > 250 °C). Anal. Found: C, 16.98; H, 4.32. $C_6H_{18}O_9P_3Rh$ calc.: C, 16.75; H, 4.19%.

Reaction of HRh{[P(OMe)$_2$O]$_2$H}$_2$(CO) with PhNCO

A solution of 0.20 g (0.35 mmol) of I in 3 ml of phenyl isocyanate was stirred at ambient temperature. Within a few min, the solution became bright yellow and a white precipitate of diphenylurea began to form. The reaction was allowed to continue for 5 d after which the reaction mixture was filtered through a 1 cc column of Celite. The bright yellow filtrate was evaporated to dryness to give 0.322 g of a pale yellow solid. The only P-containing material in the residue was $Rh\{[P(OMe)_2O]_2H\}_3$ (XIII). Attempts were made to purify XIII by fractional crystallization, but it could not be completely separated from the phenyl isocyanate decomposition products. ^{31}P NMR: δ 98.03 (d, ^{1}J(RhP) 121 Hz).

Reaction of $HRh\{[P(OMe)_2O]_2BF_2\}_2(CO)$ with PhNCO

The reaction of 0.11 g (0.16 mmol) of V and 18 μl (0.16 mmol) of phenyl isocyanate in 4 ml of chloroform-d_1 was followed by ^{31}P NMR spectroscopy. After 6 d, the ^{31}P NMR spectrum indicated that V had completely disappeared and that a number of new products had formed. The nature of these products will be discussed below.

Reaction of $[Et_4N][cis\text{-}Mo(CO)_4(PPh_2O)_2H]$ and PhNCO

A mixture of 0.30 ml of phenyl isocyanate and 0.10 g (0.16 mmol) of $[Et_4N]$[*cis*-$Mo(CO)_4(PPh_2O)_2H$] (0.10 g, 0.16 mmol) in 10 ml chloroform-d_1 was stirred at ambient temperature overnight, and then was evaporated to dryness to yield a brown residue. The ^{31}P NMR spectrum of a chloroform-d_1 solution of this material was identical to that reported for *cis*-$Mo(CO)_4(Ph_2POPPh_2)$ (XIV). ^{31}P NMR: δ 135.79 (s).

Reaction of $Et_4N^+[cis\text{-}Mo(CO)_4(PPh_2OHSPPh_2)]^-$ and PhNCO

A mixture of 0.35 ml of phenyl isocyanate and 0.10 g (0.16 mmol) of $[Et_4N]$[*cis*-$Mo(CO)_4(PPh_2OHSPPh_2)$] in 3 ml of chloroform-d_1 was stirred for 24 h at ambient temperature and then was evaporated to dryness to yield a brown solid. A ^{31}P NMR spectrum of a chloroform-d_1 solution of this material indicated that it had three major P containing components: XIV and materials giving rise to singlets in the ^{31}P NMR spectrum at 55.08 and 19.25 ppm. Attempts to separate this mixture by chromatography on silica gel resulted in the decomposition of the materials and in the formation of $Ph_2P(S)H$.

Collection and reduction of the X-ray data

A hot, saturated hexanes solution of II was slowly cooled to -10°C to yield crystals of the complex. A suitable crystal was mounted on a glass fiber with epoxy cement. Standard peak search and automatic indexing routines followed by least squares fits of 25 accurately centered reflections ($2\theta > 25°$) gave the cell constants. An Enraf-Nonius CAD-4 diffractometer with Ni-filtered Cu-K_α (λ 1.5418 Å) radiation was used for data collection. Three reflections were remeasured periodically to monitor for decay, and linear decay corrections were applied to correct for loss of intensity of 18.6% in the standards during the data collection. The data were processed using the Enraf-Nonius SDP series of programs. Variances were assigned to the Is on the basis of counting statistics with the addition of an instrumental uncertainty term. Lorentz, polarization and analytical absorption corrections were made to Is and σ^2s.

Solution and refinement of the structure

The cell parameters and systematic absences indicated that the space group was either $Pna2_1$ or $Pnma$ with the molecule on the m mirror plane. Attempts were made to refine the structure in the $Pnma$ space group, however, the Patterson function did not give positions for the P's that were related by the m mirror. Accordingly the $Pna2_1$ space group was chosen to be the correct space group, and

Table 3

Experimental data for crystallographic studies of $HRh\{[P(OMe)_2O]_2H\}_2(PPh_2Me)$ (II)

formula	$C_{21}H_{40}O_{12}P_5Rh$
MW, daltons	742.32
space group	$Pna2_1$
a, Å	19.529(1)
b, Å	13.510(1)
c, Å	12.353(4)
V, Å^3	3259.1
Z	4
d_{calc} (g/cm^3)	1.513
cryst. dim. (mm)	0.28 × 0.28 × 0.52
abs. coeff. (cm^{-1})	71.621
ext. coeff.	8.1565×10^{-7}
θ limits (°)	0.05–75
refl. meas.	3516
scan width (°)	1.14
refl. with $I > 3\sigma$	3161
No. of variables	352
R, %	6.26
R_w, %	7.60
GOF	1.516

the structure was successfully refined. Both enantiomers of II were refined, and the one giving the lower R and R_w values is reported. The Rogers test was not used to determine the correct enantiomer because the extensive decay of the crystal pre-

Table 4

Fractional coordinates with e.s.d.s for II

Atom	x	y	z	Atom	x	y	z
Rh	0.09909(2)	0.18320(3)	0.000	C3	−0.0923(5)	0.113(1)	0.044(1)
P1	0.0548(1)	0.3073(1)	0.1112(2)	C4	−0.0728(8)	0.311(1)	−0.219(2)
P2	−0.0034(1)	0.1871(2)	−0.0945(2)	C5	0.1017(8)	−0.0950(9)	0.061(1)
P3	0.1321(1)	0.0378(2)	−0.0830(2)	C6	0.2290(7)	−0.0330(9)	−0.210(1)
P4	0.1886(1)	0.1683(2)	0.1228(2)	C7	0.3223(5)	0.136(1)	0.120(1)
P5	0.16402(9)	0.2916(1)	−0.1158(2)	C8	0.186(1)	0.072(1)	0.308(1)
O1	−0.0064(4)	0.2760(6)	0.1890(6)	C9	0.2574(4)	0.2751(7)	−0.108(1)
O2	0.1062(4)	0.3584(6)	0.1866(7)	C10	0.1557(4)	0.4232(5)	−0.0874(6)
O3	0.0165(3)	0.3907(4)	0.0463(6)	C11	0.1537(4)	0.2877(7)	−0.2636(7)
O4	−0.0116(3)	0.2846(5)	−0.1617(6)	C12	0.1964(5)	0.4695(6)	−0.0094(9)
O5	−0.0703(3)	0.1952(5)	−0.0199(7)	C13	0.1140(5)	0.2173(8)	−0.3164(9)
O6	−0.0170(3)	0.0999(5)	−0.1716(6)	C14	0.1116(8)	0.216(1)	−0.428(1)
O7	0.0799(4)	−0.0086(5)	−0.1592(8)	C15	0.1461(8)	0.286(1)	−0.4864(9)
O8	0.1540(4)	−0.0486(5)	−0.0013(8)	C16	0.1888(6)	0.3596(9)	−0.3265(8)
O9	0.2019(3)	0.0495(5)	−0.1490(6)	C17	0.1831(9)	0.359(1)	−0.4385(9)
O10	0.2545(3)	0.1195(6)	0.0781(8)	C18	0.1868(8)	0.5739(8)	0.006(1)
O11	0.2119(4)	0.2647(6)	0.1743(7)	C19	0.139(1)	0.6246(9)	−0.046(1)
O12	0.1626(7)	0.0953(8)	0.2169(9)	C20	0.0988(8)	0.5790(9)	−0.116(1)
C1	0.0044(8)	0.2076(9)	0.277(1)	C21	0.1038(5)	0.4777(8)	−0.1374(9)
C2	−0.0044(7)	0.4817(8)	0.093(1)				

Table 5

Bond distances with e.s.d.s for II

Atoms	Distance	Atoms	Distance	Atoms	Distance
Rh–P1	2.333(2)	P4–O10	1.549(8)	O12–C8	1.25(2)
Rh–P2	2.317(2)	P4–O11	1.519(9)	C10–C12	1.40(1)
Rh–P3	2.307(2)	P4–O12	1.61(1)	C10–C21	1.40(1)
Rh–P4	2.323(3)	P5–C9	1.840(8)	C11–C13	1.39(1)
Rh–P5	2.408(2)	P5–C10	1.819(8)	C11–C16	1.42(1)
P1–O1	1.592(8)	P5–C11	1.837(8)	C12–C18	1.44(1)
P1–O2	1.534(8)	O1–C1	1.44(2)	C13–C14	1.38(2)
P1–O3	1.573(7)	O3–C2	1.42(1)	C14–C15	1.37(2)
P2–O4	1.565(8)	O4–C4	1.43(2)	C15–C17	1.36(2)
P2–O5	1.604(7)	O5–C3	1.43(2)	C16–C17	1.39(2)
P2–O6	1.538(7)	O8–C5	1.42(2)	C18–C19	1.33(2)
P3–O7	1.521(9)	O9–C6	1.45(1)	C19–C20	1.32(2)
P3–O8	1.601(8)	O10–C7	1.44(1)	C20–C21	1.40(2)
P3–O9	1.596(7)				

cluded the collection of both *hkl* and $-h$ $-k$ $-l$ data. The positions of the Rh and P atoms were obtained from the Patterson functions, and the remainder of the non-H atoms were located by Fourier methods. The structure was refined by a full matrix least-squares procedure that minimized $w(|F_o| - |F_c|)^2$, where $w = 1/(\sigma F_o)^2$. All non-H atoms were refined anisotropically and H atoms were included in calculated positions (staggered for methyl H's) with isotropic thermal parameters

Table 6

Bond angles with e.s.d.s. for II

Atoms	Angle	Atoms	Angle	Atoms	Angle
P1–Rh–P2	87.74(8)	Rh–P3–O7	116.0(3)	P2–O5–C3	120.4(6)
P1–Rh–P3	167.57(8)	Rh–P3–O8	114.5(3)	P3–O8–C5	118.0(8)
P1–Rh–P4	87.50(9)	Rh–P3–O9	112.4(3)	P3–O9–C6	120.2(7)
P1–Rh–P5	96.19(7)	O7–P3–O8	105.6(4)	P4–O10–C7	124.7(9)
P2–Rh–P3	92.08(9)	O7–P3–O9	107.2(4)	P4–O12–C8	134(1)
P2–Rh–P4	168.70(9)	O8–P3–O9	99.5(4)	P5–C10–C12	121.3(6)
P2–Rh–P5	98.14(7)	Rh–P4–O10	115.4(4)	P5–C10–C21	119.6(6)
P3–Rh–P4	90.37(9)	Rh–P4–O11	115.1(3)	C12–C10–C21	118.8(8)
P3–Rh–P5	96.14(8)	Rh–P4–O12	106.7(5)	P5–C11–C13	123.2(7)
P4–Rh–P5	92.56(8)	O10–P4–O11	105.4(4)	P5–C11–C16	118.1(7)
Rh–P1–O1	116.3(3)	O10–P4–O12	105.1(6)	C13–C11–C16	118.7(9)
Rh–P1–O2	116.0(3)	O11–P4–O12	108.5(5)	C10–C12–C18	117(1)
Rh–P1–O3	113.0(3)	Rh–P5–C9	114.6(4)	C11–C13–C14	120(1)
O1–P1–O2	104.2(5)	Rh–P5–C10	115.6(3)	C13–C14–C15	120(1)
O1–P1–O3	98.0(3)	Rh–P5–C11	121.0(3)	C14–C15–C17	122(1)
O2–P1–O3	107.4(5)	C9–P5–C10	101.3(4)	C11–C16–C17	120(1)
Rh–P2–O4	112.0(3)	C9–P5–C11	99.2(5)	C15–C17–C16	119(1)
Rh–P2–O5	114.6(4)	C10–P5–C11	102.1(4)	C12–C18–C19	123(1)
Rh–P2–O6	116.4(3)	P1–O1–C1	120.9(8)	C18–C19–C20	120(1)
O4–P2–O5	99.4(4)	P1–O3–C2	123.4(8)	C19–C20–C21	123(1)
O4–P2–O6	107.3(4)	P2–O4–C4	123.8(8)	C10–C21–C20	119(1)
O5–P2–O6	105.5(4)				

based upon those of the atoms to which they were attached and were not refined. The use of data with $I > 3\sigma I$ and with $0.5 < \theta < 75°$ in the refinement gave an observation to parameter ratio of 9/1. The refinement was carried out to minimize R $(\Sigma(|F_o| - |F_c|)/\Sigma|F_o|)$ and R_w $((\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{0.5})$ and to give the best goodness of fit $([\Sigma w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NN})]^{0.5})$. A secondary extinction correction of the Zachariessen type [37] was made to the data, and the extinction coefficient was refined. In the last stage of refinement no parameter varied by more than 0.03 of its standard deviation. The final difference Fourier maps had no interpretable peaks (maximum 1.375 e/Å^3). Neutral atom scattering factors were taken from the compilations of Cromer and Weber [38], and those for H atoms were taken from "International Tables for X-ray Crystallography" [39]. Corrections for the real and imaginary components of anomalous dispersion were taken from the compilations of Cromer and Liberman [40] and were applied to the Rh and P atoms. Details of the data collection and structure solution procedures are summarized in Table 3. The values for the positional parameters of II are given in Table 4, and bond lengths and angles of II are given in Tables 5 and 6.

Results and discussion

Phosphine substitution reaction

The literature procedure for the preparation of $HRh\{[P(OMe)_2O]_2H\}_2(CO)$ (I) from $Rh(CO)_2(acac)$ (acac = 2,4-pentanedionato) and an excess of $P(OMe)_2(O)H$ in hexanes gives I in poor yield [5]. However, if a stoichiometric amount of dimethylphosphite is used, I is obtained in 90% yield, as shown in eq. 1. This compound is stable in the solid state but slowly decomposes in solution to give a white solid. The decomposition product is soluble in acids but insoluble in all organic solvents. Based upon its solubility behavior, its IR spectrum and its elemental analyses, this material appears to be $Rh[P(OMe)_2O]_3$.

$$Rh(acac)(CO)_2 + 4\ H(O)P(OMe)_2 \rightarrow HRh\{[P(OMe)_2O]_2H\}_2(CO) + Hacac \qquad (1)$$

The reaction of I with $PMePh_2$, P^nBu_3 or $P(O^iPr)_3$ in either diethyl ether or THF gives nearly quantitative yields of II, III and IV, respectively, as shown in eq. 2. In contrast, I does not react with triphenylphosphine. The ^{31}P NMR spectra of II, III and IV contain doublets of doublets for the four phosphito/phosphite P's and doublets of quintets for the axial P-donor ligand. Substitution of the carbonyl by a phosphine or phosphite causes the ^{1}H NMR resonance of the hydride to shift downfield and to split into a doublet of quintets. The magnitudes of the Rh–P, Rh–H, P–P and P–H coupling constants are consistent with those reported for analogous compounds. The ^{31}P and ^{1}H NMR data indicate that these complexes contain two pairs of phosphito/phosphite ligands that are *cis* both to another P-donor ligand and to a hydride.

$$\underset{\text{(I)}}{HRh\{[P(OMe)_2O]_2H\}_2(CO)} + L \rightarrow \underset{(\text{II, L} = PPh_2Me;\ \text{III, L} = P^nBu_3;\ \text{IV, L} = P(O^iPr)_3)}{HRh\{[P(OMe)_2O]_2H\}_2(L)} + CO \qquad (2)$$

The bridging protons in the phosphito/phosphite rings are reactive and can be replaced with BF_2 groups as shown in eq. 3. The products of these reactions precipitate from ether and are stable in solution. The ^{31}P NMR spectra of V, VI and VII are similar to those of the I, II and III except that the phosphito resonances in V, VI and VII are found 4 to 7 ppm upfield of those in I, II and III and the Rh-H stretching frequencies in V, VI and VII are found 10 to 20 cm^{-1} above those of I, II and III. This suggests that replacing the bridging proton by a BF_2 group reduces the electron-donating abilities of the phosphites.

$$HRh\{[P(OMe)_2O]_2H\}_2(L) + BF_3 \cdot OEt_2 \xrightarrow{base} HRh\{[P(OMe)_2O]_2BF_2\}_2(L) \quad (3)$$

$$\begin{array}{l}(V\ (L = CO);\\ VI\ (L = PPh_2Me);\\ VII\ (L = P^nBu_3))\end{array}$$

Unlike the reaction of I with monodentate phosphines, the reactions of I with bidentate phosphines do not give single products and are complicated by the fact that the Rh complexes cause the oxidation of phosphines even when the NMR tubes are loaded in a glove box containing less than 5 ppm oxygen. Because the reaction products cannot be separated from the phosphine oxide impurities either by fractional crystallization or chromatography, ^{31}P NMR spectroscopy is the only useful method to determine the natures of the reaction products. This tool has been used successfully to study other complex reaction systems involving bis(phosphine) ligands [41].

The reaction of I with bis(diphenylphosphino)methane (dppm) proceeds very slowly with extensive decomposition and yields relatively small amounts of two products, $HRh\{[P(OMe)_2O]_2H\}_2(Ph_2PCH_2P(O)Ph_2)$ (VIII), and $Ph_2P(O)CH_2$-P(O)Ph_2. No evidence is observed for the production of the dinuclear complex, $[HRh\{[P(OMe)_2O]_2H\}_2]_2(\mu\text{-}Ph_2PCH_2PPh_2)$.

The reaction of I with bis(diphenylphosphino)ethane (dppe) is more complex. When the reaction is run with a 2/1 ratio of I to dppe in ether, both soluble and insoluble products are formed. The insoluble portion, contains primarily $[HRh\{[P(OMe)_2O]_2H\}_2]_2(\mu\text{-}Ph_2PCH_2CH_2PPh_2)$ (IX), (a doublet of doublets for the phosphite/phosphito P's and a single multiplet for the dppe P's), a material of the type $XRh(dppe)_2$ (^{31}P NMR: $\delta = 58.14$ ppm (d), $|^1J(RhP)| = 133$ Hz) [42] and some $Ph_2P(O)CH_2CH_2P(O)Ph_2$. The $XRh(dppe)_2$ material is decomposed when the insoluble material is dissolved in methanol. The soluble portion contains primarily $HRh\{[P(OMe)_2O]_2H\}_2(Ph_2PCH_2CH_2PPh_2)$ (X), (a doublet of doublets for the phosphite/phosphito P's, a multiplet for the coordinated P of the dppe and an upfield doublet for the free P of the dppe) and $HRh\{[P(OMe)_2O]_2H\}_2$-$(Ph_2PCH_2CH_2P(O)Ph_2)$ (XI), (a doublet of doublets for the phosphite/phosphito P's, a multiplet for the coordinated P of the dppe and a downfield doublet for the oxidized P of the dppe). Exposure of this mixture to pure O_2 converts all of the X to XI after several days.

The reaction of I with dppe in a 1/1 ratio gives surprisingly similar results. Even though an excess of dppe is used, the dinuclear complex IX is still formed together with the mononuclear complexes X and XI. The major difference between the two reactions is that much more of the $XRh(dppe)_2$ material is formed in the 1/1 reaction than in the 2/1 reaction. This indicates that the excess phosphine is displacing the phosphite/phosphito ligand from the complex, and thus it is not possible to obtain pure X and/or XI simply by increasing the ratio of dppe to I.

Because a dinuclear Rh complex IX is formed by the reaction of I with dppe but not with dppm, the reactions of I with bis(diphenylphosphino)butane (dppb) and with $(CO)_5W(dppe)$ were carried out. The reaction of I with dppb in a 2/1 ratio under similar conditions to those reported for the 2/1 dppe reaction does not appear to give any of the dppb coordinated products but instead results in the decomposition of I. Similarly, the reaction of I with $(CO)_5W(dppe)$ does not result in coordination of the free end of the dppe but instead oxidation of the free diphenylphosphino group occurs. These results suggest that the reaction of I with phosphines will not occur cleanly if the steric bulk of the ligands is too large.

Reactions with heteroallenes

One reason for the interest in complexes containing both a Pt-group metal hydride and a Lewis acid site is the potential for these complexes to react with CO_2 to form complexes with hydroxycarbonyl ligands bridging the Pt-group metal and Lewis acid sites. In order to determine whether I and its derivatives will function in this manner, we have studied the reactions of these complexes with CO_2 and other heteroallenes.

None of the complexes in this study react with carbon dioxide at atmospheric pressure, and, therefore, the reactions with phenyl isocyanate, a more reactive heteroallene, were studied. None of the complexes with a phosphine *trans* to the hydride (II, III, VI or VII) react with neat phenyl isocyanate. Complex I does react with excess PhNCO at ambient temperature to form $Rh\{[P(OMe)_2O]_2H\}_3$ (XIII) [5]. This complex is not formed when I is reacted with excess dimethyl phosphite, and thus the formation of XIII must require the presence of the phenyl isocyanate. Complex V also reacts with neat phenyl isocyanate. The ^{31}P NMR spectrum of the reaction mixture indicates that no hydrides are present and that the P–O–B–O–P ring is cleaved during this reaction. The reactions of I and V with phenyl isocyanate do yield products that no longer contain the hydride ligand. However, none of the products contain phenyl isocyanate-derived ligands, and thus it is not possible to determine if the reactions involve insertion of phenyl isocyanate into the Rh–hydride bond. The fact that phenyl isocyanate does not react with the complexes in which a phosphine is *trans* to the hydride, suggests that this is not the case and that the reactivity of the carbonyl complexes is due to the lability of the carbonyl ligand.

Perhaps the most surprising feature of these reactions is the lack of reactivity of the phosphite/phosphito group towards phenyl isocyanate. In order to determine if this is a general feature of complexes containing P–O–H–O–P chelate rings, the reactions of $[NEt_4][cis\text{-}Mo(CO)_4\{(PPh_2O)_2H\}]$ and $[NEt_4][cis\text{-}Mo(CO)_4\{(Ph_2PO)(Ph_2PS)H\}$ with phenyl isocyanate were carried out. The former complex reacts with a slight excess of phenyl isocyanate to form $cis\text{-}Mo(CO)_4(PPh_2OPPh_2)$ (XIV) in high yield. The latter complex reacts with a slight excess of phenyl isocyanate to form XIV and two other complexes (with ^{31}P NMR resonances at 55.08 and 19.25 ppm) in a 2/1/1 ratio. The complex giving rise to the singlet at 55.08 ppm may be $[NEt_4][cis\text{-}Mo(CO)_4\{(Ph_2PS)_2H\}]$ (XV) because of the similarity of the chemical shift of its ^{31}P NMR resonance with that of the ^{31}P NMR resonance of thiophosphinito group in the starting material (57.08 ppm) [35]. On the basis of its ^{31}P NMR chemical shift, the other material is neither $Ph_2P(S)H$ nor $cis\text{-}Mo(CO)_4(Ph_2PSPPh_2)$. Attempts to isolate this material by chromatography resulted in the decomposition of the material and the formation of $Ph_2P(S)H$. These results are consistent with the other studies that indicate that the reactivity of coordinated P-donor ligands depends greatly upon the metal to which the ligand is coordinated [1,8].

Crystal structure of HRh{[P(OMe)$_2$O]$_2$H}$_2$(PPh$_2$Me) (II)

The molecular structure of II, shown in Fig. 1, exhibits some distinct differences from those of other complexes with chelating phosphite/phosphito or phosphinite/phosphinito ligands. The coordination geometry about the Rh is a distorted octahedron with dihedral angles of 87.76(5), 91.29(5) and 89.69(6) ° between the three planes of Rh and P's and is similar to the coordination geometry of the Rh in I [4]. The four phosphite/phosphito P atoms are in a slightly puckered, square planar arrangement about the Rh ($\chi^2 = 213$) with a displacement from the least squares plane of 0.17(3) Å. The Rh is displaced 0.233(1) Å from this plane towards the PPh$_2$Me ligands. This displacement is in the opposite direction from that observed in I and is most likely a due to the fact that the PPh$_2$Me ligand in II is a good σ electron donor as is the hydride while the CO ligand in I is a good π acceptor.

The most interesting features of the structure of II are the conformations of the phosphite/phosphito chelate rings, shown in Fig. 2. As has previously been observed for other complexes with these chelate rings, the O's bonded to H in these rings are closer than the sum of their Van der Waals radii (2.426 and 2.399 Å) indicating that a strong H bond occurs between the two O's. The P and O atoms in

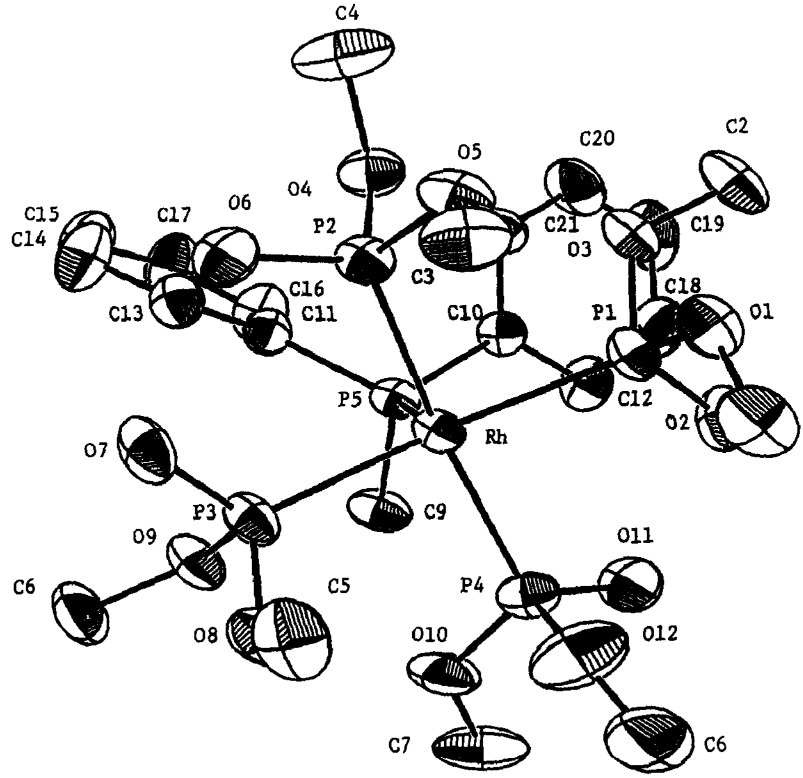


Fig. 1. ORTEP drawing [43] of the molecular structure of HRh{[P(OMe)$_2$O]$_2$H}$_2$(PPh$_2$Me) (II). All hydrogen atoms are omitted for clarity, and the thermal ellipsoids are drawn at 25% probability level.

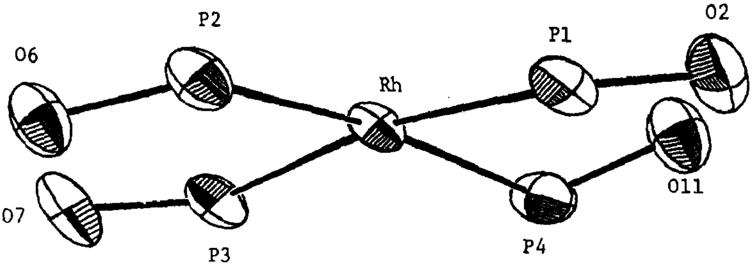


Fig. 2. ORTEP drawing [43] of the phosphite/phosphito rings in $HRh\{[P(OMe)_2O]_2H\}_2(PPh_2Me)$ (II). All hydrogen atoms are omitted for clarity, and the thermal ellipsoids are drawn at 25% probability level.

one of the rings (P2, O6, P3 and O7) are nearly coplanar ($\chi^2 = 58$, largest deviation = −0.017(8) Å), and the Rh lies only 0.071(0) Å above this plane. The P and O atoms in the other ring are not coplanar ($\chi^2 = 2154$, largest deviation = 0.100(9) Å), and the Rh lies 0.762(0) Å above this plane. These differences in planarity are reflected in the very different P–Rh–P angles of the two chelate rings (92.08(6) and 87.50(9)°). Due to the slight puckering in the plane of the four phosphite/phosphito P's, the least squares planes of the rings are not coplanar but exhibit a dihedral angle of 9(1)°. The differences in the planarity of these rings may be due to the fact that the phenyl groups of the PPh_2Me ligand, as shown in Fig. 1, are in very different orientations relative to the two rings. Complex I, containing a symmetrical CO ligand, has very similar rings with more similar P–Rh–P angles (88.64(6) and 90.80(6)°) [4].

Conclusions

Complexes of the type $HRh\{[P(OMe)_2O]_2X\}_2L$ (X = H, BF_2; L = CO, phosphine) are readily prepared in high yield. These complexes do not react with CO_2 or CS_2, but the L = CO complexes do react with phenyl isocyanate. The exact natures of these reactions are not clear although it is unlikely that they involve either a hydride reduction of the isocyanate or reaction of the isocyanate with the phosphite/phosphito groups. In contrast, phenyl isocyanate does react with phosphinite/phosphinito groups in $[NEt_4][cis\text{-}Mo(CO)_4\{(PPh_2O)_2H\}]$ and related complexes to form the expected dehydration products. The reasons for the very different reactivities of the P–O–H–O–P chelate rings in the Rh and Mo complexes is not clearly understood. The ligands in the two types of complexes do have different P substituents, and the complexes do have different charges (−1 for the Mo complex and 0 for I), however it is surprising that these differences should have such a significant effect upon the reactivities of the ligands.

The molecular structure of $HRh\{[P(OMe)_2O]_2H\}_2(PPh_2Me)$ (II) contains two very different conformations for the phosphite/phosphito rings. One of the rings is planar as has been observed in other complexes, but the other ring is significantly nonplanar. This difference may be due to the different orientations of the phenyl rings of the PPh_2Me ligand relative to the phosphite/phosphito rings.

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