ion has been estimated to be 2.22 μm^{-1}, and that of *trans*-$Pt(en)_2Cl_2^{2+}$, to be 2.25 μm^{-1} from previous luminescence experiments.[6g] Thus the reversal in the relative orders of the ^3LF and $^3\pi-\pi^*$ energies in the tetraamine complexes results from the higher ligand field strength.[22,23] The apparent proximity of the ^3LF and $^3\pi-\pi^*$ energies might be expected to lead to dual emissions from some of these species as has been reported for certain Rh(III) and Ir(III) analogues;[23] however, multiple emissions of this type could not be differentiated from those resulting from the apparent photoproduction of Pt(II) impurities.

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Registry No. *cis*-$Pt(NH_3)_2Cl_4$, 16893-05-3; $Pt(bpy)Cl_4$, 16949-85-2; $Pt(phen)Cl_4$, 17030-27-2.

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(22) For analogous Rh(III) complexes, the tetrachloro complex $Rh(phen)Cl_4^-$ displays a ^3LF emission with E^{00} about 1.6 μm^{-1}, the dichloro complexes *cis*-$Rh(phen)_2Cl_2^+$ and $Rh(bpy)_2Cl_2^+$ display ^3LF emissions with E^{00}'s about 1.9 μm^{-1}, while the tris(diimine) complexes $Rh(phen)_3^{3+}$ and $Rh(bpy)_3^{3+}$ display ligand-centered $^3\pi-\pi^*$ emissions with E^{00}'s about 2.22 μm^{-1}.[20,23,24]

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Reactions of $ReH_7(PPh_3)_2$ with 1-(Diphenylphosphino)-2-(diphenylarsino)ethane (arphos) and 1,2-Bis(diphenylarsino)ethane (dpae). Structural Characterization of $ReH_5(PPh_3)_2$(arphos-*As*) and $ReH_5(PPh_3)_2$(dpae-*As*)

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Introduction

The thermal reactions of the polyhydride complex $ReH_7(PPh_3)_2$ with monodentate σ donors (L) to form complexes of stoichiometry $ReH_5(PPh_3)_2L$ are well documented.[2-4] We have recently investigated the reactions of this complex with the bidentate donors 1-(diphenylphosphino)-2-(diphenylarsino)ethane (arphos) and 1,2-bis(diphenylarsino)ethane (dpae) with the object of probing the donor ability of the P and As atoms of the former ligand. Following the completion of our work, a publication appeared[5] that described the results of related studies on the reactions of several $ReH_7(PR_3)_2$ complexes (PR_3 = P-*i*-Pr_3, PPh_3, $P(C_6H_{11})_3$) with a range of bidentate phosphines. While the complexes isolated by Shaw and co-workers[5] differ from those that are the subject of the present report, several bear a close resemblance, in particular $ReH_5(PPh_3)_2$(dppm-*P*) and $ReH_5[P(C_6H_{11})_3]_2$(dppe-*P*), which contain monodentate $Ph_2PCH_2PPh_2$ and $Ph_2PCH_2CH_2PPh_2$, respectively. In the present report we describe the isolation and characterization of the linkage isomers $ReH_5(PPh_3)_2$(arphos-*P*) and $ReH_5(PPh_3)_2$(arphos-*As*) and of the analogous complex $ReH_5(PPh_3)_2$(dpae-*As*). Details of their NMR spectra and electrochemical properties are presented along with crystallographic data for the isostructural pair $ReH_5(PPh_3)_2$(arphos-*As*) and $ReH_5(PPh_3)_2$(dpae-*As*).

Table I. Crystallographic Data for $ReH_5(PPh_3)_2$(arphos-*As*)$\cdot 0.5C_6H_6$ (**2**) and $ReH_5(PPh_3)_2$(dpae-*As*)$\cdot 0.5C_6H_6$ (**3**)

	2	**3**
chem formula	$ReAsP_3C_{65}H_{62}$	$ReAs_2P_2C_{65}H_{62}$
fw	1197.26	1241.21
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	9.9934 (9)	10.003 (1)
b, Å	10.5311 (8)	10.571 (1)
c, Å	26.580 (3)	26.625 (3)
α, deg	99.965 (8)	99.86 (1)
β, deg	92.428 (9)	93.037 (9)
γ, deg	92.115 (7)	92.511 (9)
V, Å^3	2749.9 (9)	2766 (1)
Z	2	2
T, °C	20	20
λ(Mo Kα), Å	0.71073	0.71073
ρ_{calcd}, g cm^{-3}	1.446	1.490
μ(Mo Kα), cm^{-1}	29.59	35.06
transm coeff	1.00–0.85	1.00–0.87
R^a	0.036	0.020
$R_w{}^b$	0.046	0.027

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Experimental Section

Starting Materials. The complex $ReH_7(PPh_3)_2$ was prepared according to reported methods.[6] The ligand 1,2-bis(diphenylarisono)ethane (dpae) was purchased from Aldrich Chemical Co., while 1-(diphenylphosphino)-2-(diphenylarsino)ethane (arphos) was obtained from Strem Chemicals Inc. Both were used without further purification. All solvents were obtained from commercial sources and were deoxygenated with dinitrogen gas prior to use.

Reaction Procedures. All reactions were performed under an atmosphere of dry dinitrogen gas with the use of standard Schlenk techniques.

A. Syntheses of $ReH_5(PPh_3)_2$(arphos-*P*) (1) and $ReH_5(PPh_3)_2$(arphos-*As*) (2). This complex was obtained as an approximately 50:50 mixture of its P- and As-bound isomers. A mixture of $ReH_7(PPh_3)_2$ (0.102 g, 0.142 mmol) and arphos (0.124 g, 0.281 mmol) was refluxed in 15 mL of ethanol for 2 h. The white precipitate was filtered off, washed with ethanol (2 × 15 mL) and methanol (3 × 15 mL), and dried under vacuum; yield 0.134 g (79%). Microanalytical data were in accord with the presence of a small amount of water of crystallization. Anal. Calcd for $C_{62}H_{61}AsOP_3Re$ (i.e. $ReH_5(PPh_3)_2(arphos)\cdot H_2O$): C, 63.30; H, 5.23. Found: C, 62.28; H, 5.07. IR spectroscopy (Nujol mull) showed ν(OH) at ca. 3350 (m, br) and δ(OH) at ca. 1650 (w) cm^{-1}.

B. Synthesis of $ReH_5(PPh_3)_2$(dpae-*As*) (3). A mixture of $ReH_7(PPh_3)_2$ (0.180 g, 0.251 mmol) and dpae (0.240 g, 0.493 mmol) was refluxed in 15 mL of toluene for 2 h. The yellow solution was cooled to 0 °C, and 50 mL of pentane was added to induce precipitation of a white solid. The solid was filtered off, washed with pentane (2 × 15 mL), and dried under vacuum; yield 0.140 g (45%). Anal. Calcd for $C_{62}H_{61}As_2OP_2Re$ (i.e. $ReH_5(PPh_3)_2(dpae)\cdot H_2O$): C, 61.03; H, 5.04. Found: C, 60.14; H, 5.03. IR spectroscopy supported the presence of a small amount of water of crystallization.

When this same reaction was carried out in refluxing ethanol (same procedure as described in section A), a similar product was obtained. Anal. Found: C, 61.46; H, 5.24. However, NMR spectroscopy (in C_6D_6) showed that two products were present, one of which was **3**, and that these had very similar properties. These two products showed Re–*H* resonances as binomial triplets at δ −4.83 and −5.13, the latter being due to **3**. The $^{31}P\{^1H\}$ spectrum of this mixture was characterized by singlets at δ +37.7 and +36.8 (due to **3**).

Preparation of Single Crystals for Structure Determinations. Suitable crystals of $ReH_5(PPh_3)_2$(arphos) were obtained by the slow diffusion of pentane into a benzene solution of the mixture of P- and As-bound isomers (**1** and **2**). The best formed crystals proved to be those of **2**. A similar procedure was used to grow crystals of $ReH_5(PPh_3)_2$(dpae-*As*) (**3**) from a sample of this complex that had been prepared in ethanol.

X-ray Analysis. The structures of $ReH_5(PPh_3)_2$(arphos-*As*)$\cdot 0.5C_6H_6$ (**2**) and $ReH_5(PPh_3)_2$(dpae-*As*)$\cdot 0.5C_6H_6$ (**3**) were determined by the application of standard procedures. The basic crystallographic parameters for these complexes are listed in Table I. The cell constants were

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Table II. Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) for Non-Phenyl Atoms of **2** and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*
Re	0.06812 (3)	0.18105 (3)	0.22859 (1)	2.349 (5)
As(11)	0.00820 (9)	0.41286 (8)	0.24897 (3)	3.54 (2)
P(3)	0.2218 (2)	0.1641 (2)	0.29737 (7)	2.49 (4)
P(4)	0.0450 (2)	0.1247 (2)	0.13868 (7)	2.61 (4)
P(12)	−0.1082 (2)	0.5112 (2)	0.41691 (6)	1.59 (3)
C(11)	0.0000 (8)	0.4975 (7)	0.3205 (3)	3.2 (2)
C(12)	−0.0947 (8)	0.4244 (7)	0.3497 (3)	3.2 (2)
H(1)	0.158 (7)	0.056 (7)	0.210 (3)	1 (2)*
H(2)	0.042 (9)	0.028 (9)	0.233 (4)	4 (2)*
H(3)	−0.091 (7)	0.165 (6)	0.209 (3)	1 (1)*
H(4)	0.220 (7)	0.251 (7)	0.215 (3)	2 (2)*
H(5)	−0.044 (8)	0.189 (8)	0.275 (3)	3 (2)*

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

Table III. Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) for Non-Phenyl Atoms of **3** and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*
Re	0.07312 (1)	0.17870 (1)	0.22774 (1)	2.480 (3)
As(1)	0.01514 (4)	0.41164 (3)	0.24788 (1)	2.728 (7)
As(2)	−0.09461 (4)	0.51339 (4)	0.41972 (2)	3.553 (9)
P(3)	0.22761 (9)	0.16335 (9)	0.29697 (3)	2.63 (2)
P(4)	0.04738 (9)	0.12279 (9)	0.13791 (3)	2.74 (2)
C(1)	0.0097 (4)	0.4976 (4)	0.3199 (1)	3.28 (8)
C(2)	−0.0842 (4)	0.4237 (4)	0.3489 (1)	3.41 (8)
H(1)	0.023 (4)	0.026 (3)	0.231 (1)	1.0 (8)*
H(2)	−0.031 (4)	0.188 (4)	0.276 (1)	1.8 (9)*
H(3)	0.212 (4)	0.250 (4)	0.213 (2)	3 (1)*
H(4)	0.173 (4)	0.057 (4)	0.205 (2)	1.9 (9)*
H(5)	−0.089 (4)	0.158 (4)	0.209 (2)	3 (1)*

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

Table IV. Comparison of Important Bond Distances (Å) and Bond Angles (deg) for **2** and **3**[a]

2		**3**	
	Bond Distances		
Re–As(11)	2.5078 (9)	Re–As(1)	2.5285 (4)
Re–P(3)	2.373 (2)	Re–P(3)	2.374 (1)
Re–P(4)	2.360 (2)	Re–P(4)	2.361 (1)
Re–H(1)	1.64 (7)	Re–H(4)	1.72 (4)
Re–H(2)	1.65 (9)	Re–H(1)	1.69 (4)
Re–H(3)	1.65 (6)	Re–H(5)	1.67 (5)
Re–H(4)	1.74 (8)	Re–H(3)	1.65 (5)
Re–H(5)	1.70 (8)	Re–H(2)	1.69 (4)
	Bond Angles		
As(11)–Re–P(3)	102.16 (5)	As(1)–Re–P(3)	101.81 (3)
As(11)–Re–P(4)	105.56 (5)	As(1)–Re–P(4)	105.34 (3)
As(11)–Re–H(1)	159 (2)	As(1)–Re–H(4)	154 (1)
As(11)–Re–H(2)	151 (3)	As(1)–Re–H(1)	145 (1)
As(11)–Re–H(3)	81 (2)	As(1)–Re–H(5)	82 (2)
As(11)–Re–H(4)	82 (2)	As(1)–Re–H(3)	79 (2)
As(11)–Re–H(5)	74 (3)	As(1)–Re–H(2)	74 (1)
P(3)–Re–P(4)	140.14 (6)	P(3)–Re–P(4)	140.62 (3)
P(3)–Re–H(1)	72 (2)	P(3)–Re–H(4)	75 (1)
P(3)–Re–H(2)	80 (3)	P(3)–Re–H(1)	86 (1)
P(3)–Re–H(3)	144 (2)	P(3)–Re–H(5)	143 (2)
P(3)–Re–H(4)	73 (2)	P(3)–Re–H(3)	77 (2)
P(3)–Re–H(5)	82 (3)	P(3)–Re–H(2)	80 (1)
P(4)–Re–H(1)	71 (2)	P(4)–Re–H(4)	68 (1)
P(4)–Re–H(2)	89 (3)	P(4)–Re–H(1)	88 (1)
P(4)–Re–H(3)	69 (2)	P(4)–Re–H(5)	70 (2)
P(4)–Re–H(4)	83 (2)	P(4)–Re–H(3)	80 (2)
P(4)–Re–H(5)	133 (3)	P(4)–Re–H(2)	135 (1)
H(1)–Re–H(2)	50 (4)	H(1)–Re–H(4)	61 (2)
H(1)–Re–H(3)	116 (3)	H(4)–Re–H(5)	116 (2)
H(1)–Re–H(4)	77 (3)	H(3)–Re–H(4)	74 (2)
H(1)–Re–H(5)	124 (4)	H(2)–Re–H(4)	129 (2)
H(2)–Re–H(3)	82 (4)	H(1)–Re–H(5)	72 (2)
H(2)–Re–H(4)	125 (4)	H(1)–Re–H(3)	135 (2)
H(2)–Re–H(5)	78 (4)	H(1)–Re–H(2)	74 (2)
H(3)–Re–H(4)	141 (3)	H(3)–Re–H(5)	139 (2)
H(3)–Re–H(5)	64 (4)	H(2)–Re–H(5)	66 (2)
H(4)–Re–H(5)	141 (4)	H(2)–Re–H(3)	140 (2)

[a] Data have been arranged so as to compare related distances and angles between the two structures. Numbers in parentheses are estimated standard deviations in the least significant digits.

determined by means of least-squares analyses on 25 reflections with $16.0 < \theta < 19.0°$ for **2** and $21.0 < \theta < 23.0°$ for **3**. For each structure determination, three standard reflections were measured after every 5000 s of beam exposure during data collection; there were no systematic variations in the intensities. Calculations were performed on a micro-VAX II computer using the Enraf-Nonius structure determination package.

For both complexes the data were collected at +20 °C. The crystals of **2** and **3** were found to belong to the triclinic space group $P\bar{1}$ (No. 2). Lorentz and polarization corrections were applied to both sets of data. The structures were solved by use of the Patterson heavy-atom method, which revealed the positions of the Re atoms. The remaining nonhydrogen atoms were located in succeeding difference Fourier syntheses, including the carbon atoms of a molecule of benzene of crystallization which is located on a special position ($\bar{1}$ symmetry). Five terminally bound hydrides were tentatively located following anisotropic refinement of all non-hydrogen atoms (except for the carbons of the benzene of crystallization of **3**). Their refinement gave reasonable Re–H bond distances, and in view of the similarity of these two structures to those of other rhenium pentahydride complexes in the literature,[7,8] we are confident as to the essential correctness of the structural solutions. The positions for the hydrogen atoms of the arphos and dpae ligands, but not those of the molecules of benzene of crystallization, were calculated by assuming idealized geometries and C–H bond distances of 0.95 Å. We assumed that the value of B(H), i.e., the isotropic equivalent thermal parameter for the hydrogen atoms, was equal to $1.3[B_{eqv}(C)]$ at the time of the inclusion of this parameter in the refinement procedure. While these hydrogen atoms were used in the calculation of F_c, their positions were not refined. An empirical absorption correction was used,[9] the linear absorption coefficients being 29.59 cm^{-1} for **2** and 35.06 cm^{-1} for **3**. No corrections for extinction were applied. The structures were refined in full-matrix least squares where the function minimized was $\sum w(|F_o| - |F_c|)^2$, where w is the weighting factor defined as $w = 1/\sigma^2(F_o)$. The non-hydrogen atoms were refined anisotropically with the exception of the carbons of the molecule of benzene of crystallization of **3**; corrections for anomalous scattering were applied to all atoms so refined.[10] The largest peaks in the final difference maps (1.42 e/Å^3 for **2** and 0.54 e/Å^3 for **3**) did not appear to be of any chemical significance, since they were not at bonding distances to the atoms of the mononuclear rhenium entities.

Positional parameters and their errors for the non-phenyl group atoms of **2** and **3** are listed in Tables II and III. Some important intramolecular bond distances and angles for these two structures are compared in Table IV. Tables giving full details of the crystal data and data collection parameters (Tables S1 and S2), positional parameters for all atoms except the hydrogen atoms of the phenyl groups (Tables S3 and S4), the positional parameters for the hydrogen atoms of the phenyl groups (Tables S5 and S6), the thermal parameters (Tables S7 and S8), and complete bond distances (Tables S9 and S10) and the bond angles (Tables S11 and S12) are available as supplementary material. An ORTEP representation of the structure of **3** showing the full atomic numbering scheme (Figure S1) is also available as supplementary material.

Physical Measurements. IBM Instruments IR/32 and Perkin-Elmer 1800 FTIR spectrometers were used to record IR spectra of compounds as Nujol mulls supported on KBr plates in the region 4800–400 cm^{-1}. Electrochemical measurements were carried out by the use of a Bioa-

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(10) (a) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1. (b) For the scattering factors used in the structure solution see: Cromer, D. T.; Waber, J. T. *Ibid*, Table 2.2B.

nalytical Systems Inc. Model CV-1A instrument on dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. A Pt-bead working electrode and a Pt-wire auxiliary electrode were utilized. The $E_{1/2}$ values were determined as $(E_{p,a} + E_{p,c})/2$, referenced to the silver/silver chloride (Ag/AgCl) electrode at room temperature, and uncorrected for junction potentials. Under our experimental conditions the ferrocenium/ferrocene couple is at $E_{1/2}$ = +0.47 V vs Ag/AgCl. The ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on a Varian XL-200 spectrometer. Proton resonances were referenced internally to the residual protons in the incompletely deuteriated solvent (δ +7.20 in C_6D_6, δ +7.10 and δ +2.10 in C_7D_8, and δ +5.30 in CD_2Cl_2). Phosphorus resonances were referenced externally to 85% H_3PO_4.

Elemental microanalyses were performed by Dr. H. D. Lee of Purdue University Microanalytical Laboratory.

Results

The synthesis of $ReH_5(PPh_3)_2$(arphos-*P*) (**1**), $ReH_5(PPh_3)_2$(arphos-*As*) (**2**), and $ReH_5(PPh_3)_2$(dpae-*As*) (**3**) involved refluxing solutions of $ReH_7(PPh_3)_2$ with arphos and dpae in ethanol and toluene, respectively. Mixtures of the linkage isomers **1** and **2** were always obtained in the reaction with arphos. In the ^{1}H NMR spectra of these mixtures (recorded in C_6D_6) the P-bound form **1** displays a binomial quartet for the Re–*H* resonance at δ −5.03 ($^2J_{PH}$ = 18 Hz), while the As-bound form **2** is characterized by a binomial triplet at δ −5.13 ($^2J_{PH}$ = 19 Hz). These features are characteristic of fluxional hydride species. Over the temperature range +80 to −100 °C, the spectrum of this mixture of isomers (recorded in C_7D_8 at 200 MHz) was essentially unchanged except for a broadening of the Re–*H* resonances at the lower temperature limit. This behavior contrasts with that reported for other mononuclear rhenium pentahydride complexes,[7,8,11,12] where at low temperatures the magnetic inequivalence of the hydride ligands becomes apparent as the fluxional process is slowed. The quartet/triplet pattern in the spectra of the mixtures of **1** and **2** remains unchanged in other solvents (CD_2Cl_2 and $CDCl_3$), supporting the notion that the two chemically distinct isomers are not in equilibrium. The $-CH_2CH_2-$ resonances of the monodentate arphos ligands appear as multiplets at δ +1.75 and +2.4 in the spectra of both forms. However, the ^{31}P{^{1}H} NMR spectra of **1** and **2** (recorded in C_6D_6) are different, with resonances at δ +32.5 (PPh_3, doublet, $J_{PP} \simeq$ 16 Hz) and δ +25.0 (arphos, triplet, $J_{PP} \simeq$ 16 Hz) in the intensity ratio 2:1 for **1**, and at δ +34.5 (PPh_3, singlet, intensity 2) and δ −15.5 (arphos, singlet, intensity 1) for **2**, respectively. The large chemical shift differences for the phosphorus resonances of arphos in **1** and **2** reflect the change in coordination mode of this ligand from P- to As-bound.

The ^{1}H NMR spectrum of $ReH_5(PPh_3)_2$(dpae-*As*) (**3**) (recorded in C_6D_6) shows a binomial triplet at δ −5.13 ($^2J_{PH}$ = 20 Hz) for the Re–*H* resonance and a AA′BB′ pattern at δ +2.3 and +1.7 for the $-CH_2CH_2-$ protons of the monodentate dpae ligand. The ^{31}P{^{1}H} NMR spectrum shows a singlet at δ +36.8 due to the magnetically equivalent PPh_3 ligands.

The cyclic voltammograms of solutions **1**–**3** in 0.1 M TBAH–CH_2Cl_2 are typical of rhenium pentahydride complexes,[13,14] with irreversible oxidations being present at $E_{p,a} \simeq$ +0.2 V for **1**, $E_{p,a}$ = +0.43 V for **2**, and $E_{p,a}$ = +0.42 V for **3**; in the case of **3**, there is a coupled reduction wave at $E_{p,c}$ = +0.32 V, but $i_{p,a} > i_{p,c}$. Although IR spectroscopy was not of any great diagnostic value, the spectrum of the mixture of **1** and **2** as a Nujol mull showed ν(Re–H) modes at 1945 (w) and 1882 (2) cm^{-1}, while for **3** the ν(Re–H) bands were at 1958 (w) and 1874 (w) cm^{-1}.

The structural identity of **2** and **3** has been confirmed by single-crystal X-ray structure analyses with data collected at +20 °C. These complexes are isostructural. The ORTEP representation of **2** is shown in Figure 1, while that of **3** is available as supplementary material (Figure S1). Important intramolecular bond distances and angles for these two structures are compared in Table III. The structural refinement of **2** indicated that the asymmetric unit contained only the As-bound form of the arphos ligand; there was no evidence for disorder involving the P- and As-bound forms. The rhenium molecules possess no crystallographically imposed symmetry although the benzene of crystallization has $\bar{1}$ symmetry.

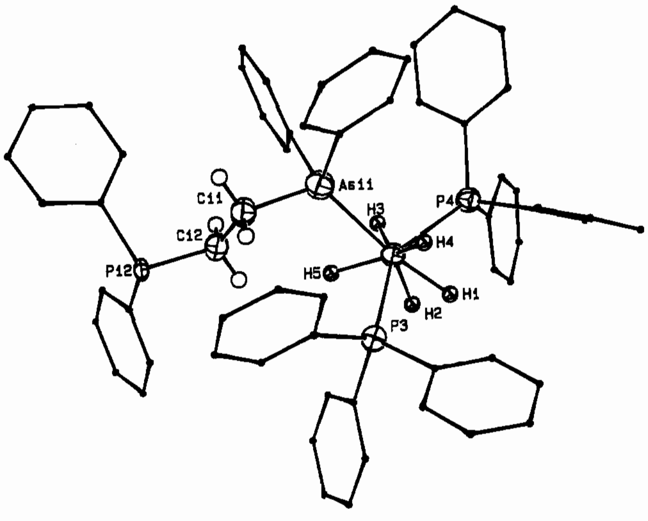

Figure 1. ORTEP representation of the structure of $ReH_5(PPh_3)_2$(arphos-*As*) (**2**) showing the atomic numbering scheme for the non-phenyl atoms. The thermal ellipsoids are drawn at the 50% probability level except for the carbon atoms of the phenyl rings, which are circles of arbitrary radius.

Discussion

The reactions of $ReH_7(PPh_3)_2$ with arphos and dpae to give $ReH_5(PPh_3)_2$(arphos-*P*) (**1**), $ReH_5(PPh_3)_2$(arphos-*As*) (**2**), and $ReH_5(PPh_3)_2$(dpae-*As*) (**3**) accord with the observations of Shaw and co-workers[5] who isolated several complexes of the type $ReH_5(PR_3)_2$(L-L-*P*), where L-L represents a potentially bidentate phosphine such as $Ph_2PCH_2PPh_2$ (dppm), $Ph_2PC(=CH_2)PPh_2$, $Ph_2PCH_2CH_2PPh_2$, or *cis*-$Ph_2PCH=CHPPh_2$. Our NMR spectral results can be compared with those reported[5] for $ReH_5(PPh_3)_2$(dppm-*P*), which like **1**–**3** is fluxional at room tempertaure, with the Re–*H* resonance appearing as a binomial quartet at δ −4.81 (in C_6D_6). Our work draws attention to two additional and noteworthy aspects of this chemistry. First, the isolation and characterization of **1** and **2** provides the first examples of linkage isomers for the rhenium polyhydrides. Second, our structural characterization of **2** and **3** affords the first unambiguous determination of the solid-state geometries of complexes of the general type $ReH_5(PR_3)_2(\eta^1$-L-L).

Data collection for the X-ray structure determinations of **2** and **3** was carried out at +20 °C with little expectation initially that the positions of the hydride ligands would be revealed. However, this proved not to be the case, since we were fortunate in growing crystals of excellent quality that afforded very good data sets. We are confident that our structural model is correct because of the close similarity of the structures of **2** and **3** to those reported for $ReH_5(PMePh_2)_3$ (from X-ray and neutron diffraction data)[7] and $ReH_5(PPh_3)_3$.[8] The X-ray structure of $ReH_5(PMe_2Ph)_3$ has also been reported,[15] although the hydride ligands were not located. The structures of **2** and **3**, like those of $ReH_5(PMePh_2)_3$[7] and $ReH_5(PPh_3)_3$,[8] are distorted dodecahedra. Since they are so similar, a brief discussion of one of them, **3**, will suffice. The geometry can be described in terms of two orthogonal trapezoidal planes, comprising As(1), H(1), H(3), H(4), and P(3), P(4), H(2), H(5), with a dihedral angle of 91.7 (7)° between the computed least-squares planes. The Re atom is displaced from the As(1), H(1), H(3), H(4) plane by only 0.02 Å but is displaced to a much greater extent (0.27 Å) in the case of the P(3), P(4), H(2), H(5) plane. The Re–P distances and the P–Re–P angles (Table IV) resemble quite closely those in related structures,[7,8,15] and the

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Re–H distances, which vary relatively little within each structure, are reasonable for M–H distances determined by X-ray crystallography.[8] Since the shortest H···H distance is 1.4 Å (H(1)–H(2) in Figure 1) and this is much longer than the value observed for η^2-H_2 complexes (ca. 0.9 Å),[16] it is clear that the present structural results signify that both **2** and **3** are "classical" hydrides.

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Supplementary Material Available: Tables giving full details of the crystal data and data collection parameters (Tables S1 and S2), positional parameters for all atoms except the hydrogen atoms of the phenyl groups (Tables S3 and S4), positional parameters for the hydrogen atoms of the phenyl groups (Tables S5 and S6), anisotropic thermal parameters (Tables S7 and S8), and complete bond distances (Tables S9 and S10) and bond angles (Tables S11 and S12) for **2** and **3** and a figure (Figure S1) showing the structure and full atomic numbering scheme for **3** (37 pages); tables of observed and calculated structure factors (85 pages). Ordering information is given on any current masthead page.

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Pressure-Induced Isomerization of a Heterometallic Rhodium–Gold Cluster Compound: $[Rh_2(\mu\text{-}Cl)_2(CNC_8H_9)_4(\mu\text{-}AuPPh_3)]_2(PF_6)_2$

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Introduction

Solid-state structural isomerization occurs when two or more configurations of a molecule or ion are of comparable stability. The existence of structural isomers reflects a delicate balance of competing intermolecular forces, and consequently the relative stability of different isomers is sensitive to minor chemical modifications (e.g. changing lattice counterions or substituent groups on ligands) and to changes in external physical parameters. High pressure is an effective tool for inducing transformations between structural isomers because high pressure is capable of altering intermolecular interactions and consequently the relative stabilities of isomers. Ferraro et al.[2,3] and Willett et al.[4] have examined the effect of pressure on five-coordinate Ni(II) and Co(II) complexes. More recently, Bray and Drickamer[5-7] have discussed pressure-induced isomerizations in several series of mononuclear Cu(II) complexes.

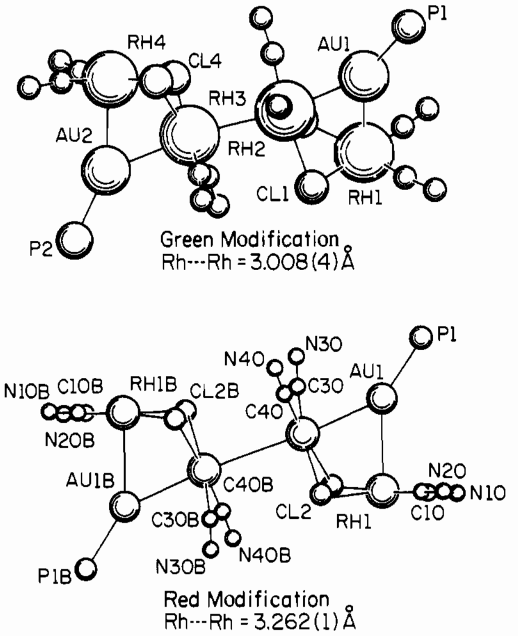

Figure 1. Structures of red and green $[Rh_2(\mu\text{-}Cl)_2(CNC_8H_9)_4(\mu\text{-}AuPPh_3)]_2(PF_6)_2$.

Structural isomerization in organometallic solids has been observed in systems ranging from mononuclear complexes to large clusters. In high-nuclearity clusters, isomers differ with respect to the skeletal arrangement of metal atoms. Mingos, for instance, has discussed isomers of the clusters $[Au_9(PR_3)_8]^{3+}$.[8,9] Two structural arrangements of the gold cluster framework were observed. When R = C_6H_5 or p-$C_6H_4CH_3$ and the anion is PF_6^-, the cluster is green and the arrangement of gold atoms may be viewed as a D_{2h} fragment of an icosahedron. A brown, D_{4d}-centered crown structure is observed when R = p-$C_6H_4OCH_3$ and the anion is BF_4^-. Coffer et al.[10] have recently discussed the first example of a pressure-induced structural transformation in a high-nuclearity metal cluster. Coffer et al.[10] demonstrated the ability of high pressure to convert the green D_{2h} form of $[Au_9(PPh_3)_8](PF_6)_3$ to the brown D_{4d} form.

In this work, we report the effect of pressure on $[Rh_2(\mu\text{-}Cl)_2(CNC_8H_9)_4(\mu\text{-}AuPPh_3)]_2(PF_6)_2$. Mingos et al. have prepared two isomers of this cluster and a characterized them using single-crystal X-ray techniques.[11] Both isomers have very similar volumes per cluster cation, viz. 1410 Å^3 (red isomer) and 1413 Å^3 (green isomer). The clusters are derived from $[Rh_2(\mu\text{-}Cl)_2(\mu\text{-}AuPPH_3)(CNC_8H_9)_4]^+$, fragments which are dimerized through a weak Rh–Rh bond (Figure 1). In the red isomer, the two cluster fragments adopt a trans, eclipsed conformation about the central Rh(2)–Rh(3) bond. A gauche, staggered conformation is observed in the green isomer. Pressure-dependent optical spectroscopy indicates that the two isomers become geometrically similar at high pressures.

Experimental Section

Synthesis of $[Rh_2(\mu\text{-}Cl)_2(CNC_8H_9)_4(\mu\text{-}AuPPh_3)]_2(PF_6)_2$. Addition of excess $TlPF_6$ to a stirred solution of $Au(PPh_3)Cl$ and $Rh(CNC_8H_9)_3Cl$ in THF yielded a dark green solution after 30 min. Removal of Tl(I) salts and subsequent addition of Et_2O gave $[Rh_2(\mu\text{-}Cl)_2(CNC_8H_9)_4(\mu\text{-}$

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