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Reactions of the Eight-Coordinate Rhenium Complex $ReH_4(hq)(PPh_3)_2$ (hq = 2-Hydroxyquinoline Monoanion) with Monodentate Tertiary Phosphines: Formation of Pentagonal Bipyramidal Dihydridorhenium(III) Complexes of the Type $ReH_2(hq)(PPh_3)_2(PR_3)$

Talia M. McKinney, Phillip E. Fanwick, and Richard A. Walton*

Department of Chemistry, Purdue University, 1393 Brown Building,
West Lafayette, Indiana 47907-1393

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The reactions of $ReH_4(hq)(PPh_3)_2$, where hq represents the monoanion of 2-hydroxyquinoline, with monodentate phosphines afford the seven-coordinate complexes $ReH_2(hq)(PPh_3)_2(PR_3)$ ($PR_3 = PMe_3$ (**1**), PMe_2Ph (**2**), $PMePh_2$ (**3**), PPh_3 (**4**), and $PHPh_2$ (**5**)) which have been shown to possess pentagonal bipyramidal structures on the basis of X-ray crystal structure determinations of **1**, **4**, and **5**. The unique PR_3 ligand occupies the pentagonal plane in the case of **1** and **5**. The reactions of **4** with PMe_3 and $PHPh_2$ lead to substitution of one of the PPh_3 ligands and the formation of **1** and **5**, respectively. The mild thermolysis of solutions of **4** in refluxing benzene affords the diphenyphosphine complex **5**, along with some decomposition of **4** and the release of free PPh_3; when this reaction is carried out in C_6D_6, the released PPh_3 is found to contain the isotopomers PPh_3-d_0 through PPh_3-d_6 with the deuteration taking place only in the ortho positions.

Introduction

The reactions of the polyhydride complex $ReH_7(PPh_3)_2$ with organic acids HA (where A represents a chelating monoanionic ligand) have been shown to produce seven-coordinate monohydridorhenium(III) complexes of the type $ReH(A)_2(PPh_3)_2$ in the cases where HA is 2-pyridinecarboxylic acid, acetylacetone, 2-hydroxypyridine, 2-mercaptopyridine, and 2-hydroxy-6-methylpyridine.[1−3] These reactions are believed to proceed in a stepwise fashion as represented in eqs 1 and 2. In the case of

$$ReH_7(PPh_3)_2 + HA \rightarrow ReH_4(A)(PPh_3)_2 + 2H_2 \qquad (1)$$

$$ReH_4(A)(PPh_3)_2 + HA \rightarrow ReH(A)_2(PPh_3)_2 + 2H_2 \qquad (2)$$

the acids 2-hydroxyquinoline (Hhq) and 2-mercaptoquinoline (Hmq), their reactions with $ReH_7(PPh_3)_2$ can be controlled to give either $ReH_4(A)(PPh_3)_2$ or $ReH(A)_2(PPh_3)_2$.[4,5] While the eight-coordinate tetrahydridorhenium(V) complexes $ReH_4(hq)(PPh_3)_2$ and $ReH_4(mq)(PPh_3)_2$ display spectroscopic and electrochemical properties which are very similar to one another,[4] they exhibit some unanticipated differences in chemical reactivity. Most noteworthy was our earlier finding that $ReH_4(mq)(PPh_3)_2$ reacts with the electrophiles H^+ and Ph_3C^+ with resulting loss of H^- and dimerization of the putative 16-e fragment $\{[ReH_3(mq)(PPh_3)_2]^+\}$.[6,7] In the presence of internal or terminal alkynes these same reactions afford salts of the novel hydridoalkylidyne cations of the type $[Re(\equiv CCH_2R)H_2(mq)(PPh_3)_2]^+$.[6] In contrast, the analogous 2-hydroxyquinoline complex $ReH_4(hq)(PPh_3)_2$ decomposes under these reaction conditions; for example, the loss of the hq ligand appears to be quite facile in H^+/CH_3CN mixtures.[4]

To establish any differences that might exist between the reactions of neutral donors with $ReH_4(hq)(PPh_3)_2$ and $ReH_4(mq)(PPh_3)_2$, we have examined the behavior of these tetrahydridorhenium(V) complexes toward monodentate phosphines (PR_3). During the course of this work, we have isolated a new class of pentagonal bipyramidal rhenium(III) complexes of the type $ReH_2(A)(PPh_3)_2(PR_3)$, where A = hq or mq and $PR_3 = PMe_3$, PMe_2Ph, $PMePh_2$, PPh_3, or $PHPh_2$. The compound $ReH_2(hq)(PPh_3)_3$ undergoes mild thermolysis to form $ReH_2(hq)(PPh_3)_2(PHPh_2)$, along with $P(C_6H_3\text{-}2,6\text{-}D_2)_3$ and other ortho-deuterated isotopomers of $P(C_6H_5)_3$ when this reaction is carried out in C_6D_6. These results are reported herein.

Experimental Section

Starting Materials and General Procedures. The tetrahydrido complexes $ReH_4(hq)(PPh_3)_2$ and $ReH_4(mq)(PPh_3)_2$ were prepared by the literature method.[4] The analogous deuteride $ReD_4(hq)(PPh_3)_2$ was obtained by a similar procedure, but with the use of $LiAlD_4$ and D_2O instead of $LiAlH_4$ and H_2O. ^1H and $^2H\{^1H\}$ NMR spectroscopy showed that the product was not isotopically pure (i.e., it was $ReH_{4-x}D_x(hq)(PPh_3)_2$ with $x \approx 3$); for simplicity it will be represented as $ReD_4(hq)(PPh_3)_2$ in all subsequent discussions. Deuterated benzene, C_6D_6 (99.6%), was obtained from Cambridge Isotope Laboratories and was used as received. Triphenylphosphine, PPh_3-d_{15}, and $LiAlD_4$ were purchased from Aldrich Chemical Co. Other phosphines were obtained from Strem Chemicals, Inc. Solvents were thoroughly deoxygenated by purging

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with dinitrogen prior to use. All reactions were performed under an atmosphere of dry dinitrogen.

A. Reactions of $ReH_4(hq)(PPh_3)_2$ with Monodentate Phosphines. The Synthesis of Complexes of the Type $ReH_2(hq)(PPh_3)_2(PR_3)$, Where PR_3 = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3, or $PHPh_2$. (i) $ReH_2(hq)(PPh_3)_2(PMe_3)$, 1. (a) A mixture of $ReH_4(hq)(PPh_3)_2$ (0.050 g, 0.058 mmol) and PMe_3 (8 μL, 0.079 mmol) was refluxed in CH_2Cl_2 (2 mL) for 1.5 h. Diethyl ether (5 mL) was added to the reaction mixture to precipitate a dark orange solid. This solid was filtered off, washed with diethyl ether (3 × 5 mL), and dried under vacuum; yield 0.035 g (60%). Anal. Calcd for $C_{48.75}H_{48.5}Cl_{1.5}NOP_3Re$ (i.e., $ReH_2(hq)(PPh_3)_2(PMe_3)\cdot 0.75CH_2Cl_2$): C, 58.69; H, 4.87. Found: C, 58.82; H, 4.90. ^{1}H NMR spectroscopy showed the presence of a small quantity of lattice CH_2Cl_2. If the reaction is carried out at room temperature for 24 h and worked up as described above, **1** is produced in similar yield (65%).

(b) A mixture of $ReH_2(hq)(PPh_3)_3$ (see A(iv)) (0.025 g, 0.022 mmol) and PMe_3 (3 μL, 0.0295 mmol) was stirred at room temperature in C_6H_6 (3 mL) for 20 h. The solvent was removed by use of a vacuum, and $CH_2Cl_2/(C_2H_5)_2O$ (2 mL/15 mL) was added to precipitate an orange solid, which was filtered off, washed with diethyl ether (3 × 5 mL), and dried under vacuum; yield 0.015 g (67%).

(ii) $ReH_2(hq)(PPh_3)_2(PMe_2Ph)$, 2. A mixture of $ReH_4(hq)(PPh_3)_2$ (0.050 g, 0.058 mmol) and PMe_2Ph (26 μL, 0.182 mmol) was stirred in CH_2Cl_2 (5 mL) at room temperature for 24 h. A bright orange solid, which precipitated from the solution, was filtered off and dried under vacuum; yield 0.041 g (69%). Anal. Calcd for $C_{53.25}H_{49.5}Cl_{0.5}NOP_3Re$ (i.e., $ReH_2(hq)(PPh_3)_2(PMe_2Ph)\cdot 0.25CH_2Cl_2$): C, 62.93; H, 4.87. Found: C, 62.90; H, 4.88. ^{1}H NMR spectroscopy showed the presence of a small quantity of lattice CH_2Cl_2.

(iii) $ReH_2(hq)(PPh_3)_2(PMePh_2)$, 3. The use of a procedure similar to A(ii) afforded this compound as a pale orange solid; yield 59%. Anal. Calcd for $C_{58.25}H_{51.5}Cl_{0.5}NOP_3Re$ (i.e., $ReH_2(hq)(PPh_3)_2(PMePh_2)\cdot 0.25CH_2Cl_2$): C, 64.88; H, 4.78. Found: C, 64.56; H, 4.98. ^{1}H NMR spectroscopy showed the presence of a small amount of lattice CH_2Cl_2.

(iv) $ReH_2(hq)(PPh_3)_3$, 4. A mixture of $ReH_4(hq)(PPh_3)_2$ (0.200 g, 0.233 mmol) and PPh_3 (0.244 g, 0.930 mmol) in C_6H_6 (5 mL) was stirred at room temperature for 24 h. After most of the solvent had been removed by use of a vacuum, pentane (10 mL) was used to precipitate a dark orange solid. This solid was filtered off, washed with pentane, and dried under vacuum; yield 0.144 g (55%). Anal. Calcd for $C_{63}H_{53}NOP_3Re$: C, 67.61; H, 4.77. Found: C, 67.98; H, 4.97.

When $ReH_4(hq)(PPh_3)_2$ was stirred at room temperature in benzene, in the absence of added PPh_3, for periods of between 20 and 48 h, $ReH_2(hq)(PPh_3)_3$ was formed in small amounts. With longer reaction times, both the tetrahydride starting material and the product **4** decomposed to give appreciable quantities of free PPh_3 and $OPPh_3$.

(v) $ReH_2(hq)(PPh_3)_2(PHPh_2)$, 5. (a) A mixture of $ReH_4(hq)(PPh_3)_2$ (0.100 g, 0.116 mmol) and $PHPh_2$ (0.51 mL of a 0.274 M solution in benzene, 0.140 mmol) was stirred at room temperature in C_6H_6 (5 mL) for 64 h. A red-orange slurry resulted. The orange solid was filtered off, washed with diethyl ether (3 × 5 mL), and dried under vacuum; yield 0.066 g (55%). Alternatively, this same product was isolated in 46% yield, after workup, when these reagents were refluxed for 1 h.

(b) A mixture of $ReH_4(hq)(PPh_3)_2$ (0.200 g, 0.233 mmol) and PPh_3 (0.244 g, 0.930 mmol) in 5 mL of C_6H_6 was refluxed for 20 h. The benzene was removed by the use of a vacuum, and a mixture of CH_2Cl_2 and $(C_2H_5)_2O$ (2 mL/15 mL) was added to precipitate an orange solid, which was filtered off, washed with diethyl ether (3 × 5 mL), and dried under vacuum; yield 0.102 g (40%). Anal. Calcd for $C_{57.5}H_{50}ClNOP_3Re$ (i.e., $ReH_2(hq)(PPh_3)_2(PHPh_2)\cdot 0.5CH_2Cl_2$): C, 63.59; H, 4.61. Found: C, 63.64; H, 4.55. ^{1}H NMR spectroscopy showed the presence of a small amount of lattice CH_2Cl_2.

This same reaction was carried out under conditions which allowed for the monitoring of the formation of free $PHPh_2$. A mixture of $ReH_4(hq)(PPh_3)_2$ (0.030 g, 0.035 mmol) and PPh_3 (0.037 g, 0.141 mmol) in C_6H_6 (0.5 mL) was sealed under vacuum in a NMR tube. This tube was heated at 84 °C (oil bath) for 30 h. The reaction solution was monitored over time by the use of ^{31}P{^{1}H} NMR spectroscopy. The resonance for free $PHPh_2$ (at $\delta = -40.3$) was not detected during the course of this reaction.

(c) A quantity of $ReH_4(hq)(PPh_3)_2$ (0.050 g, 0.058 mmol) was refluxed in benzene (5 mL) for 5.5 h. The solvent was removed by the use of a vacuum, and $CH_2Cl_2/(C_2H_5)_2O$ (1 mL/15 mL) was added to the residue to precipitate an orange solid. This solid was filtered off, washed with diethyl ether (3 × 5 mL), and dried under vacuum; yield 0.013 g (21%).

(d) A mixture of $ReH_2(hq)(PPh_3)_3$, **4** (0.100 g, 0.089 mmol), and $PHPh_2$ (0.49 mL of a 0.274 M solution in benzene, 0.134 mmol) was stirred at room temperature in C_6H_6 (5 mL) for 24 h. The solvent was removed by the use of a vacuum, and $CH_2Cl_2/(C_2H_5)_2O$ (2 mL/15 mL) was added to the residue to precipitate an orange solid. This solid was filtered off, washed with diethyl ether (3 × 5 mL), and dried under vacuum; yield 0.060 g (64%).

(e) $ReH_2(hq)(PPh_3)_3$, **4** (0.010 g, 0.009 mmol), was refluxed in benzene (2 mL) for 1 h to produce a red-orange solution. The solvent was removed by the use of a vacuum, and the residue was found to contain an appreciable quantity of **5** (yield ca. 40%) as established by NMR spectroscopy.

B. Reactions of $ReH_4(mq)(PPh_3)_2$ with Monodentate Tertiary Phosphines. The Synthesis of Complexes of the Type $ReH_2(mq)(PPh_3)_2(PR_3)$, Where PR_3 = PMe_3, PMe_2Ph, $PMePh_2$, or PPh_3. These complexes were obtained as oily residues and were identified by NMR spectroscopy. One representative reaction only is described. A mixture of $ReH_4(mq)(PPh_3)_2$ (0.100 g, 0.114 mmol) and PMe_3 (14.2 μL, 0.140 mmol) was refluxed in C_6H_6 (10 mL) for 7 h. The solvent was removed by the use of a vacuum. The resulting red-purple residue was treated with CH_2Cl_2/hexane (1 mL/15 mL). No solid formed, and the red solution was evaporated to an oily residue by the use of an aspirator. This residue was found to contain an appreciable quantity of $ReH_2(mq)(PPh_3)_2(PMe_3)$, **6**.

The compounds where PR_3 = PMe_2Ph (**7**), $PMePh_2$ (**8**), and PPh_3 (**9**) were obtained by the use of procedures very similar to that described for **6**.

C. Deuterium Labeling Reactions. (i) The Formation of $ReH_2(hq)(PPh_3)_2(PHPh_2)$ (5) and Deuterated PPh_3. (a) A mixture of $ReD_4(hq)(PPh_3)_2$ (0.050 g, 0.058 mmol) and PPh_3 (0.060 g, 0.229 mmol) was refluxed in 3 mL of C_6H_6 for 24 h. The solvent was removed by the use of a vacuum. The residue contained $ReH_2(hq)(PPh_3)_2(PHPh_2)$, **5** (yield ca. 30%), as well as PPh_3, PPh_3-d_1, and $OPPh_3$ as shown by ^{1}H, ^{2}H{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy.

(b) A mixture of $ReD_4(hq)(PPh_3)_2$ (0.050 g, 0.058 mmol) and PPh_3 (0.060 g, 0.229 mmol) was refluxed in C_6D_6 (3 mL) for 24 h. An aliquot of this reaction solution was used for NMR spectral analysis. Deuterium was found to be incorporated into the phosphine ligands of **5**, as evidenced by broadening of the doublet and triplet resonances in the ^{31}P{^{1}H} NMR spectrum (C_6D_6) due to the various isotopomers which are present. Deuterium was also incorporated into the free PPh_3 to give isotopomers up to PPh_3-d_3.

(c) A mixture of $ReH_4(hq)(PPh_3)_2$ (0.050 g, 0.058 mmol) and PPh_3-d_{15} (0.040 g, 0.144 mmol) was refluxed in C_6H_6 (5 mL) for 22 h. A sample was analyzed by ^{31}P{^{1}H} NMR spectroscopy and was found to contain resonances due to **4** and **5** (ca. 1:2 ratio) in addition to deuterated PPh_3 and a small amount of $OPPh_3$; all resonances were broadened because of deuterium incorporation into the phosphine ligands. The ^{2}H{^{1}H} NMR spectrum of this sample did not display resonances due to the presence of Re−D bonds or the $PDPh_2$ ligand.

(d) A quantity of $ReH_2(hq)(PPh_3)_3$, **4** (0.050 g, 0.045 mmol), was refluxed in 2 mL of C_6D_6 for 2.5 h. An aliquot of the reaction solution was analyzed by the use of NMR spectroscopy (C_6D_6) and mass spectrometry. This sample contained $ReH_2(hq)(PPh_3)_2(PHPh_2)$ (yield ca. 20%, with no unreacted starting material present) and PPh_3 along with isotopomers up to PPh_3-d_6. A similar result was obtained when this reaction was carried out in the absence of light.

(e) A mixture of $ReH_2(hq)(PPh_3)_3$, **4** (0.050 g, 0.0447 mmol), and PPh_3 (0.0059 g, 0.0225 mmol) (i.e., 2:1 proportions) was refluxed in C_6D_6 (2 mL) for 2.5 h. An aliquot was analyzed by the use of NMR spectroscopy. Compound **5** was produced (yield 20%), and the free PPh_3 showed deuterium incorporation (up to d_4).

When this same reaction was carried out with a mole ratio for **4**:PPh_3 of 1:2 (instead of 2:1), compound **5** was produced in much lower yield (ca. 5%) along with PPh_3 isotopomers up to d_3. With larger excesses of PPh_3, essentially no reaction of **4** occurred under these same reaction conditions.

(ii) The Formation of $ReH_{5-x}D_x(PPh_3)_3$. A mixture of ReH_2(hq)$(PPh_3)_3$, **4** (0.025 g, 0.022 mmol), $LiAlD_4$ (0.0095 g, 0.226 mmol), and PPh_3 (0.018 g, 0.069 mmol) was refluxed in 3 mL of C_6H_6 for 2.5 h. The products included $ReH_{5-x}D_x(PPh_3)_3$ (yield ca. 70%) in addition to small amounts of PPh_3, PPh_3-d_1, and PPh_3-d_2, but no unreacted starting material remained. The $^2H\{^1H\}$ NMR spectrum (C_6H_6) showed a broadened resonance at δ −4.8 assigned to the deuterium in $ReH_{5-x}D_x(PPh_3)_3$. When $LiAlH_4$ was used in the above reaction, $ReH_5(PPh_3)_3$ was produced in a similar yield.

X-ray Crystallography. Single crystals of composition ReH_2(hq)$(PPh_3)_2(PMe_3)$·THF (**1**) were grown at 25 °C under a dinitrogen atmosphere from a mixed THF/hexane solution by slow evaporation of the solvents, while crystals of ReH_2(hq)$(PPh_3)_3$ (**4**) and ReH_2(hq)$(PPh_3)_2(PHPh_2)$ (**5**) were grown under similar such conditions by the diffusion of hexane and heptane, respectively, into benzene solutions of the complexes. The data collections for **1** and **4** were performed on an Enraf-Nonius diffractometer equipped with a graphite monochromator, and for **5** on a Nonius KappaCCD diffractometer. Data were collected at 296 K for **1** and **4** and at 156 K for **5**. The cell constants were based on 25 reflections obtained randomly in the ranges $23° < 2\theta < 45°$ for **1**, $40° < 2\theta < 46°$ for **4**, and $12° < 2\theta < 43°$ for **5**, as measured by the computer-controlled diagonal slit method of centering. Three standard reflections were measured after every 5000 s of beam time during the data collection to monitor the stability of the crystals. The intensities of these standard reflections remained constant within experimental error throughout the data collections. Lorentz and polarization corrections were applied to the data sets.

The structures were solved by a combination of direct methods (DIRDIF92)[8] and difference Fourier syntheses. The two hydride ligands were located in the Fourier map and refined with isotropic thermal parameters. The hydrogen atoms bound to carbon were placed in calculated positions according to idealized geometries with C−H = 0.95 Å and $U(H) = 1.3U_{eq}(C)$. They were included in the refinement but constrained to ride on the atom to which they are bonded. Calculations were performed on an AlphaServer 2100 computer. The final refinements were performed by the use of the programs MolEN[9] for **1** and **4** and SHELXL-97[10] for **5**.

All non-hydrogen atoms in **1** and **4** were refined with anisotropic thermal parameters with the exception of the THF solvent molecule present in **1**; the atoms of THF were all treated as C and refined isotropically. An empirical absorption correction was applied in the case of **1** and **4**.[11] These two structures were refined in full-matrix least squares where the function minimized was $\sum w(|F_o| - |F_c|)^2$ and the weighting factor w is defined as $w = 4F_o^2/\sigma^2(F_o^2)$. The highest peaks in the final difference Fouriers of **1** and **4** were 0.88e and 0.39 e/Å^3, respectively, while the minimum negative peaks were −0.25 and −0.16 e/Å^3, respectively.

Two independent molecules of **5** were present in the asymmetric unit. All non-hydrogen atoms were refined with anisotropic thermal parameters. No absorption correction was applied. The two hydride ligands and the secondary phosphine hydrogen atom present in each of the independent molecules were located in the Fourier map and refined with fixed isotropic thermal parameters. The structure was refined in full-matrix least squares where the function minimized was $\Sigma w(|F_o|^2 - |F_c|^2)^2$ and the weighting factor w is defined as $w = 1/[\sigma^2(F_o^2) + (0.1236P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. The highest peak in the final difference Fourier of **5** was 2.01 e/Å^3, and the minimum negative peak was −1.74 e/Å^3.

The crystallographic data for compounds **1**, **4**, and **5** are given in Table 1, while important intramolecular bond lengths and angles are compared in Table 2.

Physical Measurements. The ^1H, ^{31}P, and $^{31}P\{^1H\}$ NMR spectra were recorded with the use of a Varian XL-200A or QE-300 spectrometer. Proton resonances were referenced internally to residual protons in the incompletely deuterated solvents (CD_2Cl_2, δ = +5.35; $CDCl_3$, δ = +7.25; and C_6D_6, δ = +7.15). The phosphorus resonances were referenced externally to a sample of 85% H_3PO_4; an internal lock was used. The $^2H\{^1H\}$ NMR spectra were recorded with the use of a Varian XL-200A spectrometer and a tunable probe.[6] A Perkin-Elmer 1800 FTIR or 2000 FTIR spectrophotometer was used to record the IR spectra of compounds as KBr pellets or Nujol mulls between NaCl or KBr plates. Mass spectral data were obtained by Arlene P. Rothwell and Dr. Karl V. Wood of the Purdue University Campus-Wide Mass Spectrometry Center. The positive chemical ionization mass spectra were measured on a Hewlett-Packard 5989 gas chromatograph/mass spectrometer with a 30 m HP-5 column. The injection temperature was 250 °C, and the column temperature ramped 10°/min from 100 to 250 °C. Isobutane was used as the reagent gas, and helium was the carrier gas. Voltammetric experiments were performed with a Bioanalytical Systems Inc. (BAS) Model CV-27 instrument in conjunction with a BAS Model RXY recorder. Dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte were used for the electrochemical measurements. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the silver/silver chloride (Ag/AgCl) electrode at room temperature and were uncorrected for junction potentials. Under our experimental conditions, $E_{1/2}$ = +0.47 vs Ag/AgCl for the ferrocenium/ferrocene couple. Conductivity measurements were carried out on acetone solutions of the complexes (ca. 1 × 10^{-3} M) with use of a Yellow Springs Instrument Co., Inc., Model 35 conductance meter. Elemental microanalyses were determined by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

Table 1. Crystallographic Data for the Complexes ReH_2(hq)$(PPh_3)_2(PMe_3)$·THF, **1**, ReH_2(hq)$(PPh_3)_3$, **4**, and ReH_2(hq)$(PPh_3)_2(PHPh_2)$, **5**

	1	**4**	**5**
empirical formula	$ReP_3O_2NC_{52}H_{55}$	$ReP_3ONC_{63}H_{53}$	$ReP_3ONC_{57}H_{49}$
fw	1005.14	1119.25	1043.15
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
a, Å	12.240(2)	17.932(2)	45.685(4)
b, Å	12.411(3)	12.819(1)	12.211(1)
c, Å	15.196(3)	22.290(1)	36.400(6)
α, deg	93.20(2)		
β, deg	93.90(1)	101.84(1)	114.92(1)
γ, deg	96.22(2)		
V, Å^3	2284.9(14)	5014.9(13)	18416(8)
Z	2	4	16
ρ_{calcd}, g/cm^3	1.461	1.484	1.505
μ, mm^{-1}	6.320	5.817	2.818
radiation (λ, Å)	Cu Kα (1.541 84)	Cu Kα (1.541 84)	Mo Kα (0.710 73)
transm factors, min/max	0.36/0.68	0.33/0.56	
temp, K	296	296	156
$R(F_o)^a$	0.038	0.029	0.061
$R_w(F_o^2)^b$	0.049	0.039	0.224
GOF	1.372	1.034	1.013

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

Results and Discussion

(a) Synthesis and Characterization of Complexes of the Type $ReH_2(A)(PPh_3)_2(PR_3)$, Where A = hq or mq. The complex ReH_4(hq)$(PPh_3)_2$ reacts at room temperature with monodentate phosphine ligands PR_3, where PR_3 = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3, or $PHPh_2$, in dichloromethane or benzene to

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Table 2. Comparison of Selected Bond Distances (Å) and Bond Angles (deg) for $ReH_2(hq)(PPh_3)_2(PMe_3)\cdot THF$, **1**, $ReH_2(hq)(PPh_3)_3$, **4**, and $ReH_2(hq)(PPh_3)_2(PHPh_2)$, **5**[a]

	1		**4**		**5**[b]
		Distances			
Re−P(2)	2.3828(13)	Re−P(3)	2.4023(11)	Re(1)−P(1)	2.383(3)
Re−P(1)	2.3692(13)	Re−P(1)	2.3900(11)	Re(1)−P(3)	2.355(3)
Re−P(3)	2.3615(14)	Re−P(2)	2.4126(11)	Re(1)−P(2)	2.349(3)
Re−O(2)	2.247(3)	Re−O(2)	2.254(3)	Re(1)−O(12)	2.264(9)
Re−N(1)	2.180(4)	Re−N(1)	2.172(3)	Re(1)−N(11)	2.171(9)
Re−H(1)	1.75(4)	Re−H(1)	1.66(5)	Re(1)−H(12)	1.90(6)
Re−H(2)	1.61(5)	Re−H(2)	1.47(5)	Re(1)−H(11)	1.90(6)
				P(2)−H(2)	1.35(9)
		Angles			
P(1)−Re−P(2)	173.95(5)	P(1)−Re−P(3)	168.94(4)	P(1)−Re(1)−P(3)	174.19(12)
P(2)−Re−P(3)	92.86(5)	P(3)−Re−P(2)	94.97(4)	P(1)−Re(1)−P(2)	99.09(11)
P(1)−Re−P(3)	92.43(5)	P(1)−Re−P(2)	94.81(4)	P(3)−Re(1)−P(2)	84.98(11)
P(3)−Re−O(2)	92.55(9)	P(2)−Re−O(2)	96.55(8)	P(2)−Re(1)−O(12)	96.9(2)
P(3)−Re−N(1)	152.44(10)	P(2)−Re−N(1)	156.03(10)	P(2)−Re(1)−N(11)	156.3(3)
N(1)−Re−O(2)	59.90(13)	N(1)−Re−O(2)	59.48(12)	N(11)−Re(1)−O(12)	60.0(4)
				Re(1)−P(2)−H(2)	116(5)

[a] Comparisons are made between corresponding parameters in the three structures as represented by the labeling schemes in Figures 1−3. [b] Data are given for one of the two independent molecules in the asymmetric unit.

Table 3. Selected NMR Spectral Data and Electrochemical Properties for Dihydride Complexes of the Type $ReH_2(A)(PPh_3)_2(PR_3)$

complex			chem shift, δ[a]		CV half-wave potentials, V[b]	
A	PR_3	no.	^1H NMR: Re−H	$^{31}P\{^1H\}$ NMR	$E_{p,a}$	$E_{1/2}(ox)$[c]
hq	PMe_3	**1**	−7.28 (d of t; 13 Hz, 32 Hz)	+22.2 (d, 12.5 Hz); −18.6 (t, 12.5 Hz)	+0.52	−0.17 (65)
hq	PMe_2Ph	**2**	−7.32 (d of t; 13 Hz, 30 Hz)	+21.3 (d, 11.1 Hz); −0.69 (t, 11.1 Hz)	+0.51	−0.15 (65)
hq	$PMePh_2$	**3**	−7.55 (d of t; 13.5 Hz, 30 Hz)	+22.0 (d, 10.9 Hz); +14.1 (t, 10.9 Hz)	+0.53	−0.14 (60)
hq	PPh_3	**4**	−6.94 (d of t; 12.5 Hz, 30 Hz)	+22.1 (d, 10.5 Hz); +31.9 (t, 10.5 Hz)	+0.72	−0.17 (60)
hq	$PHPh_2$	**5**	−7.43 (d of t; 13 Hz, 32 Hz)	+24.1 (d, 11.5 Hz); +17.5 (t, 11.5 Hz)	+0.68	−0.06 (65)
mq	PMe_3	**6**	−6.09 (d of t; 14 Hz, 34 Hz)	+20.3 (d, 11.6); −31.7 (t, 11.6)		
mq	PMe_2Ph	**7**	−5.64 (d of t; 16.5 Hz, 32.5 Hz)	+19.4 (d, 11.5 hz); −11.5 (t, 11.5 Hz)		
mq	$PMePh_2$	**8**	−5.63 (m)	+21.5 (d, 11.5 Hz); + 8.67 (t, 11.5 Hz)		
mq	PPh_3	**9**	−6.17 (m)	+20.9 (d, 11.8 Hz); +14.6 (m)		

[a] NMR spectra recorded at room temperature on C_6D_6 solutions of the complexes except for **2** and **9**, whose spectra were recorded in $CDCl_3$ and CD_2Cl_2, respectively. Abbreviations: d of t = doublet of triplets, t = triplet, d = doublet, m = multiplet. [b] Measured on 0.1 M TBAH/CH_2Cl_2 solutions and referenced to the Ag/AgCl electrode with a scan rate (ν) of 200 mV/s at a Pt-bead electrode. Under our experimental conditions, $E_{1/2} = +0.47$ V for the ferrocenium/ferrocene couple. [c] Numbers in parentheses are the values of $E_{p,a} - E_{p,c}$ (in mV) for this process with a switching potential of ca. +0.3 V.

afford the orange complexes of composition $ReH_2(hq)(PPh_3)_2(PR_3)$ in isolated yields of 55% or more (eq 3). Use of

$$\begin{aligned} ReH_4(hq)(PPh_3)_2 + PR_3 \rightarrow ReH_2(hq)(PPh_3)_2(PR_3) + H_2 \\ PR_3 = PMe_3\ (\mathbf{1}) \\ PMe_3Ph\ (\mathbf{2}) \\ PMePh_2\ (\mathbf{3}) \\ PPh_3\ (\mathbf{4}) \\ PHPh_2\ (\mathbf{5}) \end{aligned} \tag{3}$$

dichloromethane as the reaction solvent usually led to small amounts of lattice solvent being present in the products. In the case of $PR_3 = PMe_3$, PMe_2Ph, $PMePh_2$, or $PHPh_2$, reflux conditions did not significantly affect the product or product yield, although much shorter reaction times can be used. However, when the reaction between $ReH_4(hq)(PPh_3)_2$ and PPh_3 was carried out in refluxing benzene for periods of several hours, the major product was not $ReH_2(hq)(PPh_3)_3$ (**4**) but rather the diphenylphosphine complex **5**, i.e., P−C bond breaking involving free or coordinated PPh_3 had occurred. Details of this particular reaction, and other reactions which were carried out in an attempt to elucidate the mechanism for the transformation of PPh_3 to $PHPh_2$, are discussed in section b.

While the reactions of monodentate tertiary phosphines with the mq analogue of $ReH_4(hq)(PPh_3)_2$ produced complexes of the type $ReH_2(mq)(PPh_3)_2(PR_3)$, where $PR_3 = PMe_3$ (**6**), PMe_2Ph (**7**), $PMePh_2$ (**8**), and PPh_3 (**9**), these were only isolated in oily residues and identified on the basis of the close similarity of their NMR spectral properties to those of **1**−**4** (see Table 3). Their chemistry was not pursued further.

The structures of three of the complexes of the type $ReH_2(hq)(PPh_3)_2(PR_3)$ ($PR_3 = PMe_3$ (**1**), PPh_3 (**4**) and $PHPh_2$ (**5**)) were determined by X-ray crystallography. ORTEP[12] representations of the structures of **1**, **4**, and **5** are shown in Figures1−3 and reveal that all possess a very similar pentagonal bipyramidal geometry with two PPh_3 ligands in the trans axial sites. A comparison of the most important structural parameters is presented in Table 2. The structure of **5** contains two independent molecules in the asymmetric unit; since these possess essentially identical parameters, only those for one of the molecules is given in Table 2. The pair of trans PPh_3 ligands have P−Re−P angles in the range 169−175°; the smallest angle (169°) is found in the case of **4**, which has the most sterically demanding PR_3 ligand (PPh_3) in the pentagonal plane. Each of the pentagonal planes of **1**, **4**, and **5** contains a chelating hq ligand (N−Re−O angle of ca. 60°), two hydride ligands, and a PR_3 ligand approximately trans to the N atom of the hq ligand (the P−Re−N angles in the plane are in the range 152−156°).

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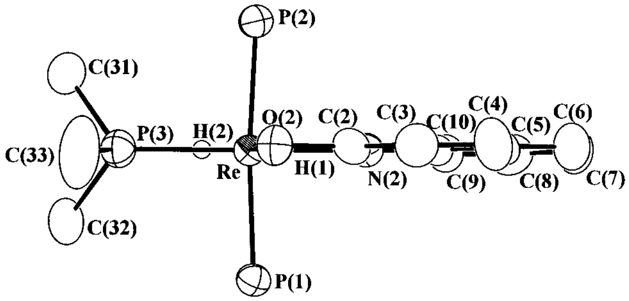

Figure 1. ORTEP[12] representation of the structure of the seven-coordinate complex $ReH_2(hq)(PPh_3)_2(PMe_3)$ (**1**) to emphasize the planarity of the $ReH_2(hq)(PMe_3)$ unit. The hydride ligand H(1) is obscured by the Re and O(2) atoms. Atoms P(1) and P(2) are those of the PPh_3 ligands, the phenyl groups of which have been omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level except for the hydride ligands, which are represented as circles of arbitrary radius.

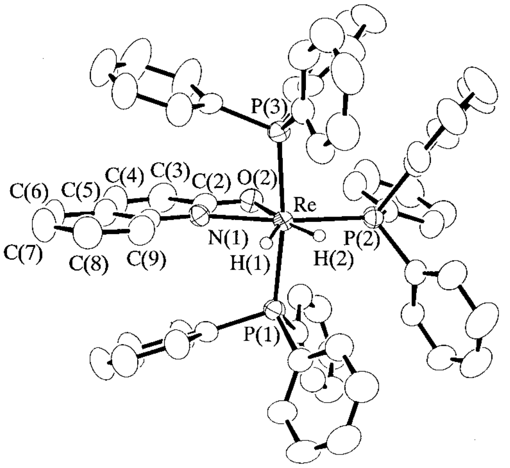

Figure 2. ORTEP[12] representation of the structure of the seven-coordinate complex $ReH_2(hq)(PPh_3)_3$ (**4**). The thermal ellipsoids are drawn at the 50% probability level except for the hydride ligands, which are represented as circles of arbitrary radius.

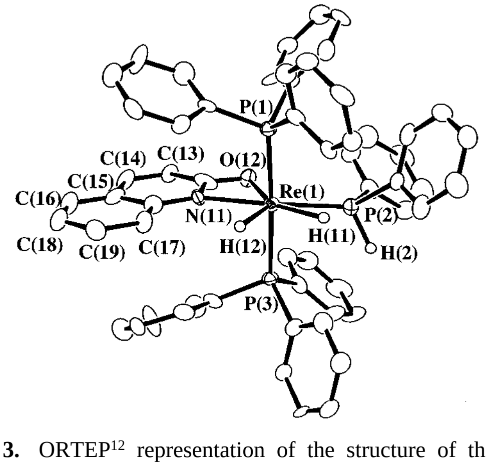

Figure 3. ORTEP[12] representation of the structure of the seven-coordinate complex $ReH_2(hq)(PPh_3)_2(PHPh_2)$ (**5**). The thermal ellipsoids are drawn at the 50% probability level except for the hydride ligands and the hydrogen atom of the P−H group, which are represented as circles of arbitrary radius.

The Re, P (of the PR_3 ligand), O, N, all carbon atoms of the hq ligand, and the two hydrides all lie in a plane; the greatest deviation from planarity for **1** is 0.173(57) Å (atom H(1)), for **4**, it is 0.188(46) Å (atom H(1)), and for **5**, is 0.207(4) Å (atom P(2)). The Re−P distance for the PPh_3 ligand in the pentagonal plane of **4** is only slightly longer than the Re−P distances for the pair of axial PPh_3 ligands. While the hydrido ligands were located in the difference map and refined with isotropic thermal parameters, the Re−H bond distances and H−Re−H angles are not considered accurate enough to merit further discussion. The comparable bond length and bond angle data for the non-hydrogen atoms of **1**, **4**, and **5** are essentially identical within the limits of 3σ (Table 2), signifying the very close similarity of all three structures.

The room temperature ^1H NMR spectra of the 2-hydroxyquinoline complexes **1**−**5** show a multiplet for the Re−*H* resonance which has the appearance of an approximate doublet of triplets (Table 3). This pattern is consistent with a rigid structure for the three phosphine ligands as present in the solid state (Figures 1−3). The remaining features in the ^1H NMR spectra consist of phenyl ring resonances between $\delta = +8.0$ and $\delta = +7.0$ and a sharp doublet at $\delta =$ ca. $+6.0$ that is characteristic of the chelating hq ligand. The $^{31}P\{^1H\}$ NMR spectra of **1**−**5** display two resonances, a doublet and a triplet with J_{P-P} ca. 12 Hz (Table 3). The doublet is assigned to the pair of trans PPh_3 ligands, the triplet to the unique in-plane PR_3 ligand; as expected, the resonance for the latter ligand is phosphine dependent and occurs over a wide chemical shift range (from $\delta = -19$ to $+32$).

Variable-temperature NMR spectra were measured on solutions of **1** and **5** in CD_2Cl_2 over the range +30 to −70 °C (in 10 deg intervals). The room-temperature spectra in CD_2Cl_2 are very similar to those obtained in C_6D_6 (see Table 3). The $^{31}P\{^1H\}$ NMR spectrum of **1** in CD_2Cl_2 changes very little over this temperature range, although both the doublet and triplet progressively shift downfield, the former from $\delta = +21.8$ to $+21.0$ and the latter, assigned to the in-plane PMe_3 ligand, from $\delta = -18.6$ to -16.9. The Re−*H* resonance at $\delta = -7.69$ (approximate doublet of triplets) remains quite sharp and well resolved down to −20 °C, although it has shifted upfield to $\delta = -8.05$ by the time this temperature has been reached. Further cooling results in a broadening and splitting of this resonance into two broad humps ($\delta =$ ca. -8.3 and ca. -8.75), indicating that the apparent equivalence of the hydride ligands at room temperature is removed at low temperature although the $ReNOP_3$ skeleton remains rigid throughout this temperature range. Temperature range $^{31}P\{^1H\}$ NMR data, similar to that observed in the case of **1**, were found for the analogous $PHPh_2$ complex **5**. The doublet at $\delta = +23.6$ and triplet at $\delta = +19.1$ for CD_2Cl_2 solutions of **5** (at +30 °C) are found at $\delta = +23.7$ and $+24.3$, respectively, when the temperature is lowered to −70 °C. The downfield shift of the triplet resonance is similar to that observed in the temperature range spectra of **1**. While we are unsure as to the explanation for this phenomenon, it is not due to exchange with free phosphine as shown by measurements of the $^{31}P\{^1H\}$ NMR spectra of solutions of **1** and **5** in the presence of added PMe_3 or $PHPh_2$, respectively. The ^1H NMR spectrum of **5** at +30 °C consists of a broadened, poorly resolved doublet-of-triplets pattern centered at $\delta =$ ca. -7.75; upon lowering the temperature to −70 °C it takes on the appearance of a broadened plateau but does not resolve into two separate resonances.

Each of the IR spectra of **1**−**5** (recorded as Nujol mulls) shows a pair of weak/very weak bands between 2000 and 2060 cm^{-1} which we assign to the ν(Re−H) modes. Also of note is a pair of very sharp, weak bands at 2266 and 2258 cm^{-1} in the IR spectrum of **5** which can be attributed to ν(P−H) modes of the coordinated $PHPh_2$ ligand in the two crystallographically independent molecules that are present in the crystals of **5**.

Conductivity measurements on acetone solutions of **1**−**5** ($c_m = 1 \times 10^{-3}$ M) confirm these complexes to be nonelectrolytes ($\Lambda_m < 5\ \Omega^{-1}$ cm^2 mol^{-1}). Cyclic voltammetric measurements on solutions of **1**−**5** in 0.1 M *n*-Bu_4NPF_6/CH_2Cl_2 show that each compound exhibits a reversible process between −0.06 and −0.17 V vs Ag/AgCl, corresponding to a one-electron oxidation of the bulk complex, and an irreversible oxidation in the range +0.5 to +0.75 V. The similarity of the CV's again signifies the close structural relationship of these complexes.

(b) The Conversions of $ReH_4(hq)(PPh_3)_2$ and $ReH_2(hq)(PPh_3)_3$ to $ReH_2(hq)(PPh_3)_2(PHPh_2)$. The synthesis of the diphenylphosphine complex $ReH_2(hq)(PPh_3)_2(PHPh_2)$ (**5**) is most conveniently accomplished by the reaction of $ReH_4(hq)(PPh_3)_2$ with $PHPh_2$ (eq 3). However, we also observe its formation (in ca. 40% yield) both from the reaction between $ReH_4(hq)(PPh_3)_2$ and an excess of PPh_3, upon prolonged reflux of benzene, and when benzene solutions of the complex $ReH_2(hq)(PPh_3)_3$ (**4**) are refluxed for ca. 1 h. Since **5** is also produced in low yield (ca. 20%) upon heating $ReH_4(hq)(PPh_3)_2$ solutions in benzene for a few hours, *in the absence of added* PPh_3, it is apparent that some portion of the tetrahydride must decompose to release free PPh_3 into solution under these conditions. This is confirmed by our finding that $ReH_2(hq)(PPh_3)_3$ is formed when $ReH_4(hq)(PPh_3)_2$ is stirred alone in benzene at room temperature for long periods. The conversion of coordinated PPh_3 to $PHPh_2$ has been documented previously in the literature. Examples include the reaction of $ReH_7(PPh_3)_2$ with 2,6-dimethylbenzenethiolate in toluene to produce $Re(DMT)_3(PPh_3)(PHPh_2)$, via the presumed intermediacy of an $(\eta^6\text{-}C_6H_5)PPh_2$ ligand.[13] The compound $CoH(CO)_3(PHPh_2)$ is produced from $Co_2(CO)_8$ by a mechanism which is believed to involve P−C bond cleavage of PPh_3.[14]

Since **5** is formed in yields lower than 50% by all procedures other than the reaction of $ReH_4(hq)(PPh_3)_2$ with $PHPh_2$ (eq 3), and the fate of an appreciable quantity of the original rhenium polyhydride starting materials is unknown, a detailed mechanistic study of the thermal conversion of $ReH_4(hq)(PPh_3)_2/PPh_3$ mixtures and $ReH_2(hq)(PPh_3)_3$ to $ReH_2(hq)(PPh_3)_2(PHPh_2)$ was not justified. Nonetheless, several conclusions are possible.

(1) The observation that benzene solutions both of $ReH_4(hq)(PPh_3)_2/PPh_3$ mixtures and $ReH_2(hq)(PPh_3)_3$ (**4**) convert to **5** confirms that **4** is the starting complex for the formation of **5**.

(2) A key step in the conversion of **4** to **5** involves the dissociation of the PPh_3 ligand of **4** which lies in the pentagonal plane (see Figure 2). This is supported by our observation that this PPh_3 ligand is easily displaced by PMe_3 and $PHPh_2$ to produce **1** and **5**, respectively, in good yield at room temperature. The axial PPh_3 ligands are not displaced even in the presence of a large excess of PR_3. As expected, the conversion of **4** to **5** is dramatically retarded when solutions of **4** are heated in the presence of a large excess of PPh_3. At room temperature, benzene solutions of $ReH_2(hq)(PPh_3)_3$ decompose over a period of 24 h to release PPh_3; the addition of excess PPh_3 to **4** suppresses this decomposition. Compound **4** is the only complex of the type $ReH_2(hq)(PPh_3)_2(PR_3)$ to exhibit this phosphine lability.

(3) By monitoring the conversion of a $ReH_4(hq)(PPh_3)_2/PPh_3$ mixture to **5** by $^{31}P\{^1H\}$ NMR spectroscopy we were able to show the absence of detectable quantities of free $PHPh_2$. However, this observation does not distinguish between an intramolecular mechanism for the formation of **5** and one in which free $PHPh_2$ is involved since **4** reacts rapidly with $PHPh_2$ to form **5**, thereby precluding the buildup of measurable quantities of free $PHPh_2$ in the system.

(4) The thermal conversion of **4** to **5** is not dependent upon the presence of light. Also, low levels of oxygen have little effect, but deliberate exposure of solutions of **4** to O_2 leads to their decomposition and the conversion of released PPh_3 to $OPPh_3$.

On the basis of the aforementioned observations, we conclude that the conversion of **4** to **5** involves as a first step the dissociation of a PPh_3 ligand to afford the reactive 16-electron intermediate $[ReH_2(hq)(PPh_3)_2]$, followed perhaps by orthometalation of a phenyl ring of one of the two remaining PPh_3 ligands to generate $ReH_3(hq)(o\text{-}C_6H_4PPh_2)(PPh_3)$, and its subsequent conversion to $ReH_2(hq)(PPh_3)(PHPh_2)(\eta^2\text{-}C_6H_4)$, and finally $ReH_2(hq)(PPh_3)_2(PHPh_2)$ (with loss of benzyne) upon recoordination of PPh_3. Presumably, benzyne loss from $[ReH_2(hq)(PPh_3)_2]$ is possible without the intermediacy of an oxidative-addition step. While we were unable to find evidence to support the participation of benzyne in this reaction in the benzene solvent, this possibility is certainly plausible given the precedent for forming benzyne from a coordinated PPh_3 ligand; examples include the formation of $Os_3(CO)_7(PPh_2)_2(C_6H_4)$,[15] $Ir_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}OH)(\mu\text{-}PPh_2)(\mu\text{-}C_6H_4)$,[16] and $[Ir_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}C_6H_4)]$.[17]

(c) Deuterium Labeling Experiments. In an attempt to trace the source of the H in the $PHPh_2$ ligand of **5** when this complex is formed by the thermolysis of **4**, several deuterium labeling experiments were conducted. As mentioned previously, a major portion of the rhenium starting material ($ReH_4(hq)(PPh_3)_2$ or $ReH_2(hq)(PPh_3)_3$) does not end up as the desired product **5** but rather as ill-defined decomposition products. Therefore, there seem to be two competing pathways; the dissociation of a PPh_3 ligand allows for the conversion of **4** to **5** but also leads to the decomposition of **4** to unidentified species, both routes proceeding through the intermediacy of $[ReH_2(hq)(PPh_3)_2]$.

When $ReD_4(hq)(PPh_3)_2$ was reacted with an excess of PPh_3 in refluxing C_6H_6 to produce **5**, we found little evidence from $^2H\{^1H\}$ NMR spectroscopy for Re−D bonds being present in the product. In addition, ^{31}P NMR spectroscopy indicated the absence of the $PDPh_2$ ligand in **5**. The ^{31}P NMR spectrum of $ReH_2(hq)(PPh_3)_2(PHPh_2)$ (**5**) shows a broad "doublet" for the $PHPh_2$ resonance at $\delta = +17.5$ with $J_{P-H} =$ ca. 364 Hz; a similar spectrum should have been observed in the case of $ReH_2(hq)(PPh_3)_2(PDPh_2)$ but with a much smaller coupling constant (J_{P-D}).[18] The *free* PPh_3 which remains at the end of the reaction between $ReD_4(hq)(PPh_3)_2$ and PPh_3 was found to contain some $PPh_3\text{-}d_1$ (as evidenced by $^{31}P\{^1H\}$ NMR). We suggest that the formation of **5** by this route involves loss of D from the $ReD_2(hq)(PPh_3)_3$ intermediate through oxidative addition/reductive elimination reactions involving the C−H bonds of PPh_3. This result led us to carry out the reaction between $ReD_4(hq)(PPh_3)_2$ and PPh_3 in refluxing C_6D_6; workup of the reaction mixture obtained under these conditions showed that PPh_3 was present as a mixture of isotopomers $PPh_3\text{-}d_0$ to $PPh_3\text{-}d_3$. Clearly, the presence of a deuterium source from the solvent enhances the incorporation of D into the free PPh_3 but does not prevent the loss of D bound to the metal, in accord with our suggested

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mechanism for the formation of **5**. To ascertain the nature of the PPh_3-d_n isotopomers we used $^{31}P\{^1H\}$ NMR spectroscopy in combination with mass spectrometry (MS). Siedle and Newmark[19] have shown that the substitution of each ortho H by D in free PPh_3 produces an upfield shift of 0.11 ppm in the 161 MHz $^{31}P\{^1H\}$ NMR spectra. On the other hand, substitution of the meta and para protons resulted in negligible shifts.[19] To establish whether meta and para substitution had also occurred, we resorted to MS studies of the PPh_3-containing reaction residues. In all cases mentioned above, and in others to be discussed below, there was no evidence for the buildup of deuterium in excess of that determined to be present in the ortho positions. Furthermore, there was good agreement between $^{31}P\{^1H\}$ NMR spectroscopy and MS as to the relative proportions of PPh_3-d_n isotopomers.

Further studies have established that the formation of free ortho-deuterated PPh_3 (d_1 to d_6) is maximized when $ReH_2(hq)(PPh_3)_3$ is refluxed in C_6D_6 for 2.5 h *in the absence of added* PPh_3. In addition to the formation of **5**, the $^{31}P\{^1H\}$ NMR spectra of the reaction residue showed the presence of isotopomers d_0 to d_6 (see Figure S1); the seven resonances span the range $\delta = -4.85$ to -5.51 and are separated by 0.11 ($\pm$ 0.01) ppm. The MS of this sample (using isobutane chemical ionization) showed a relative intensity pattern for the $(M + H)^+$ parent peaks very similar to that found for the isotopomers from $^{31}P\{^1H\}$ NMR spectrometry, viz., d_0 (6%), d_1 (5%), d_2 (13%), d_3 (26%), d_4 (27%), d_5 (18%), and d_6 (5%) (see Figure S2). It was also established that ca. 56% of the six ortho positions of PPh_3 were deuterated in this sample. Since peaks within the $(M + H)^+$ cluster with *m/z* values greater than 269 (i.e., greater than $[PPh_3 + H + 6]^+$) were not present, deuterium incorporation into the meta and para positions of the phenyl groups of PPh_3 had not occurred.

When mixtures of $ReH_2(hq)(PPh_3)_3$ (**4**), $LiAlD_4$, and PPh_3 were refluxed in C_6H_6 (or C_6D_6), small amounts of PPh_3-d_1 and PPh_3-d_2 were generated along with the very stable and unreactive mixed pentahydride/deuteride complex $ReH_{5-x}D_x(PPh_3)_3$, which once it has formed shows no further reactivity. Under conditions similar to these, mixtures of **4**, $LiAlH_4$, and PPh_3 afford high yields of the known complex $ReH_5(PPh_3)_3$.[21]

As we have mentioned above, the conversion of **4** to **5** requires the lability of the equatorial PPh_3 ligand of the former complex, and this is also the case with the formation of the PPh_3-d_n isotopomers. This was confirmed by control experiments in which the complexes $ReH_2(hq)(PPh_3)_2(PMe_3)$ (**1**) and $ReH_2(hq)(PPh_3)_2(PHPh_2)$ (**5**) were recovered quantitatively unchanged from their solutions in refluxing C_6D_6, as were mixtures of the complex $ReOCl_3(PMe_3)_2$[20] and PPh_3 in refluxing C_6D_6. Accordingly, it is only during the conversion of **4** to **5** in C_6D_6 that PPh_3-d_n is formed; this presumably requires oxidative addition/reductive elimination steps involving both ligated PPh_3 and C_6D_6, since the deuterium which is incorporated into the free PPh_3-d_n must originate from the C_6D_6 solvent. We believe that these observations are most satisfactorily explained by two separate processes. The first is the conversion of **4** to **5** via the 16-electron intermediate $[ReH_2(hq)(PPh_3)_2]$, and the second is the ortho deuteration of free PPh_3 by an unidentified species *which is formed from that portion of* ***4*** *which decomposes and does not end up as product* ***5***. The first process does not involve the solvent while the second process requires the presence of C_6D_6.

One final reaction which we studied was that between $ReH_4(hq)(PPh_3)_2$ and PPh_3-d_{15} in refluxing C_6H_6. A combination of $^{31}P\{^1H\}$ and $^2H\{^1H\}$ NMR spectroscopy showed that while a mixture of **4** and **5** had been formed, in the case of **4** the equatorial PPh_3 ligand was not exclusively PPh_3-d_{15}, i.e., PPh_3 ligand scrambling had occurred in the conversion of $ReH_4(hq)(PPh_3)_2$ to **4**. Consistent with this observation was our finding that the PPh_3-containing residue was not pure PPh_3-d_{15}. The absence of stereospecificity can be attributed to the fluxionality of the $ReH_4(hq)(PPh_3)_2$, starting material and the lability of the equatorial PPh_3 ligand of **4** which permits scrambling of the three PPh_3 ligands via the 16-electron intermediate $[ReH_2(hq)(PPh_3)_2]$. In contrast, the use of phosphines other than PPh_3, i.e., PMe_3, PMe_2Ph, $PMePh_2$ and $PHPh_2$, leads exclusively to the isomer with the unique PR_3 ligand in the pentagonal plane.

Concluding Remarks

Although both $ReH_4(hq)(PPh_3)_2$ and $ReH_4(mq)(PPh_3)_2$ react with monodentate phosphine ligands (PR_3) to form the seven-coordinate complexes $ReH_2(hq)(PPh_3)_2(PR_3)$ and $ReH_2(mq)(PPh_3)_2(PR_3)$, the latter proved to be rather intractable and their chemistry was not examined in any detail. Structure determinations on three complexes of the type $ReH_2(hq)(PPh_3)_2(PR_3)$ ($PR_3 = PMe_3$ (**1**), PPh_3 (**4**), or $PHPh_2$ (**5**)) have shown that these complexes possess pentagonal bipyramidal geometries in the solid state and that in solution the $[Re(hq)(PPh_3)_2(PR_3)]$ moiety retains its rigid structure. The PR_3 ligand of **4** dissociates thereby leading to the instability of this complex in solution; however, its stability is enhanced in the presence of an excess of added PPh_3. Mild thermolysis of **4** in C_6H_6 results in its conversion to **5**, along with some unidentified rhenium-containing decomposition products and PPh_3. When this reaction is carried out in C_6D_6, the released PPh_3 contains a mixture of ortho-deuterated isotopomers PPh_3-d_1 through PPh_3-d_6. The key to this chemistry appears to lie in the intermediacy of the 16-electron intermediate $[ReH_2(hq)(PPh_3)_2]$, formed through dissociation of a PPh_3 ligand.

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Supporting Information Available: $^{31}P\{^1H\}$ NMR and mass spectra for the PPh_3-containing residue from workup of the reaction mixture obtained by refluxing $ReH_2(hq)(PPh_3)_3$ in C_6D_6. X-ray crystallographic files in CIF format for complexes **1**, **4**, and **5** are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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