(Bis(pyrazolyl)methane)heptahydridorhenium(VII) (4). To a suspension of $BpReOCl_3$ (1.09 g, 3 mmol) in thf (30 mL) at 25 °C was added $LiAlH_4$ (900 mg, 24 mmol). After 2 h, the solvent was removed in vacuo, and the light yellow residue was suspended in toluene (30 mL). Hydrolysis by slow addition of water (0.5 mL) at 0 °C led to the formation of the title complex (**4**), which was isolated by evaporation of the toluene, extraction of the residue with CH_2Cl_2, reduction of the volume of the CH_2Cl_2 solution, and precipitation of the analytically pure material with diethyl ether. Yield: 83 mg, 8%. Anal. Calcd for $C_7H_{15}N_6N_4Re$: C, 24.61; H, 4.40; N, 16.41. Found: C, 24.87; H, 4.38; N, 16.26. ^1H NMR (CD_2Cl_2, 298 K): δ 8.00 (d, J_{HH} = 2.3 Hz, 2 H, pz), 7.73 (d, J_{HH} = 2.3 Hz, 2 H, pz), 6.49 (s, 2 H, CH_2), 6.35 (t, J_{HH} = 2.3 Hz, 2 H, pz, 4-proton), -2.52 (s, 7 H, Re-H). ^1H NMR (CD_2Cl_2/CF_3Cl, 178 K): δ 7.90 (br s, 2 H, pz), 7.60 (br s, 2 H, pz), 6.33 (s, 2 H, CH_2), 6.35 (br s, 2 H, pz, 4-proton), 3.14 (br s, 2 H, Re-H, T_1 = 75 ms), -5.00 (br s, 5 H, Re-H, T_1 = 75 ms). IR (Nujol): ν_{Re-H} 2128 (m), 2024 (m), 2000 (s), 1922 cm^{-1} (w).

T_1 and Isotope Shift Measurements

T_1 measurements were made as described in ref 5, at 250 MHz in CD_2Cl_2 at 200 K. T_1 minima were not observed for either **1** or **4** in the accessible temperature range.

The isotopomeric mixtures of **1**, **2**, and **4** were prepared by treatment of the corresponding precursors with $LiAlH_4/LiAlD_4$ (1:4 molar ratio) followed by hydrolysis with H_2O/D_2O (1:4 molar ratio). The isotope shifts, defined as $\Delta\delta = \delta_{ReH_{x-1}D_{y+1}L_z} - \delta_{ReH_xD_yL_z}$, are reported as follows: temperature (K), isotope shifts (in ppm/D and in Hz/D at 250 MHz). No isotope effect (<0.002 ppm/D) could be observed for **4**.

1: 298, -0.0247, -6.18; 293, -0.0253, -6.32; 283, -0.0265, -6.62; 273, -0.0271, -6.77; 263, -0.0282, -7.06; 253, -0.0294, -7.35; 2438 -0.0303, -7.54; 233, -0.0311, -7.79; 223, -0.0323, -8.09; 213, -0.0338, -8.46; 203, -0.0353, -8.82. **2**: 298, -0.0304, -7.72; 283, -0.0323, -8.09; 273, -0.0341, -8.53; 263, -0.0360, -9.01; 253, -0.0379, -9.53; 243, -0.0397, -10.00; 233, -0.0416, 10.48; 223, -0.0434, -10.88; 213, -0.0453, -11.33; 203, -0.0470, -11.76.

Attempts To Observe Alkane Conversion

Alkane activation experiments with **1** and **4** were performed as described in ref 15, with cyclooctane as substrate and solvent and *t*-$BuCH{=}CH_2$ as hydrogen acceptor at 25, 80, and 130 °C in a sealed glass vessel. No cyclooctene was detected, and decomposition of the complexes occurred at 130 °C, forming black precipitates.

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Reactions of the Dirhenium(II) Complexes $Re_2Cl_4(PR_3)_4$ with Lithium Aluminum Hydride. A Convenient Synthetic Route to the Dirhenium Octahydride Complexes $Re_2H_8(PR_3)_4$

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A general synthetic method has been developed for the preparation of dirhenium octahydride complexes of the type $Re_2H_8(PR_3)_4$ that is adaptable to PR_3 being a trialkylphosphine, a mixed alkylarylphosphine, or a bidentate phosphine; i.e., PR_3 = PMe_3, PEt_3, P-*n*-Pr_3, PMe_2Ph, PEt_2Ph, $PMePh_2$, $Ph_2PCH_2PPh_2$ (dppm), or $Ph_2PCH_2CH_2PPh_2$ (dppe). This procedure involves the reaction of the triply bonded species $Re_2Cl_4(PR_3)_4$ with $LiAlH_4$ in glyme (or THF) at room temperature, followed by hydrolysis of the reaction mixture. These reactions probably proceed by a mechanism that involves the retention of the dirhenium unit throughout. The formation of the mononuclear heptahydride complexes $ReH_7(PR_3)_2$ as byproducts in some of these reactions can be attributed to the further reaction of $LiAlH_4$ with $Re_2H_8(PR_3)_4$ with resulting disruption of the dimetal unit. In the case of the PMe_3 complex, this is a convenient method for preparing $ReH_7(PMe_3)_2$. The crystal structure and NMR spectral properties of the dppm derivative are consistent with the structure $Re_2(\mu\text{-}H)_2H_6(\mu\text{-dppm})_2$, rather than $Re_2(\mu\text{-}H)_4H_4(\mu\text{-dppm})_2$. The complex of stoichiometry $Re_2H_8(dppm)_2$ crystallizes in the monoclinic space group $P2_1/n$ with a = 12.962 (3) Å, b = 12.002 (8) Å, c = 14.979 (4) Å, β = 112.30 (2)°, V = 2156 (3) Å^3, and Z = 2. The structure, which was refined to R = 0.048 (R_w = 0.057) for 2470 data with $I > 3.0\sigma(I)$, reveals an unexpectedly long Re-Re bond (2.933 (1) Å) and a P-Re-P angle (164.1 (1)°) much larger than is observed in structurally characterized derivatives with monodentate phosphines. The complex $Re_2H_8(dppe)_2$ probably contains chelating phosphine ligands but is otherwise closely related structurally to the complexes that contain monodentate phosphines.

Introduction

The syntheses of the dirhenium octahydride complexes $Re_2H_8(PR_3)_4$ (PR_3 = PEt_2Ph or PPh_3) were first reported by Chatt and Coffey in 1969,[1] and the diethylphenylphosphine derivative was structurally characterized as $Re_2(\mu\text{-}H)_4H_4(PEt_2Ph)_4$ by Bau et al.[2] in 1977. Since that time, a few additional derivatives of this type have been prepared, most notably $Re_2H_8(PMe_2Ph)_4$,[3] but no uniform synthetic strategy has been developed. The original Chatt and Coffey procedure,[1] namely the thermal decomposition of the corresponding mononuclear heptahydride complexes $ReH_7(PR_3)_2$, requires that these heptahydride starting materials be available and that they not be thermally resistant to loss of H_2 and dimerization, a condition that is not always met.[4] Several other reactions have been described in which dirhenium octahydride complexes are formed: (1) the reaction of $(n\text{-}Bu_4N)_2Re_2Cl_8$ or $Re_2Cl_6(PPh_3)_2$ with $NaBH_4$ and PPh_3 in ethanol to give $Re_2H_8(PPh_3)_4$;[5,6] (2) the photolysis of $ReH_5(PR_3)_3$ or $ReH_7(PR_3)_2$ (PR_3 = PPh_3, $PMePh_2$, or PMe_2Ph) to give $Re_2H_8(PR_3)_4$, along with several other products;[7,8] (3) the chemical oxidation of $K[ReH_6(PMePh_2)_2]$ to form $Re_2H_8(PMePh_2)_4$;[9] (4)

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the reaction of $ReCl_5$ with PMe_3 and $LiAlH_4$ in an ether solvent to give $Re_2H_8(PMe_3)_4$.[10] However, not all of these reactions have been developed into useful synthetic procedures, and no single procedure has been adapted to a wide range of phosphine ligands.

In this report, we describe a single uniform synthetic strategy that is applicable for use with monodentate and bidentate phosphine ligands. This procedure utilizes the triply bonded dirhenium(II) complexes $Re_2Cl_4(PR_3)_4$ as the key starting materials[11,12] and has been successfully used to prepare the corresponding hydrido complexes $Re_2H_8(PR_3)_4$ in the case of PR_3 = PMe_3, PEt_3, P-*n*-Pr_3, PMe_2Ph, PEt_2Ph, $PMePh_2$, $Ph_2PCH_2PPh_2$ (dppm), and $Ph_2PCH_2CH_2PPh_2$ (dppe). The properties of the resulting complexes are described herein, along with a report on the X-ray crystal structure of $Re_2H_8(dppm)_2$. A preliminary report of some of these results has been published.[13]

Experimental Section

Starting Materials. Standard literature procedures were used to prepare the complexes $Re_2X_4(PR_3)_4$ (X = Cl or Br; PR_3 = PMe_3,[14] PEt_3,[11] P-*n*-Pr_3,[11] PMe_2Ph,[11] PEt_2Ph,[11] or $PMePh_2$[15]) and $Re_2X_4(LL)_2$ (X = Cl or Br; LL = dppm[16] or dppe[12]). All solvents and other reagents were obtained from commercial sources. Glyme was distilled from Na/benzophenone before use. Other solvents were dried with standard techniques and deoxygenated by a nitrogen purge.

Reaction Procedures. All reactions and manipulations were performed under a dry nitrogen atmosphere by using standard vacuum-line techniques. A 3-ft 18-gauge cannula was used for transferring many of the reaction mixtures.

A. Reactions of $Re_2X_4(PR_3)_4$ and $Re_2X_4(LL)_2$ with Lithium Aluminum Hydride (LAH). For the following reactions, the synthesis of $Re_2H_8(PMe_3)_4$ is described in full detail. Details for the other syntheses are provided only insofar as the workups differ from that used in the purification of $Re_2H_8(PMe_3)_4$.

(i) $Re_2H_8(PMe_3)_4$. A quantity of LAH (0.397 g, 10.458 mmol) was added slowly with stirring to $Re_2Cl_4(PMe_3)_4$ (0.534 g, 0.652 mmol) in 20 mL of glyme. The mixture was then stirred at room temperature for 17 h, and the resulting gray suspension was hydrolyzed with a mixture of 5 mL of deoxygenated H_2O and 15 mL of glyme. The resulting orange mixture was stirred with gentle warming for an additional 4 h and then filtered through Celite, with a cannula used for transfer of the solution. The dark orange filtrate was stripped dry under vacuum. The residue was extracted into benzene and filtered through Celite to remove a purple solid residue, and the filtrate was again evaporated to dryness. The orange residue that resulted was redissolved in a small volume of methanol and filtered into an excess of deoxygenated H_2O ($\simeq$150 mL), again with a cannula used for transfer. The orange precipitate was filtered off, washed with H_2O, and dried under vacuum; yield 0.150 g (34%). Anal. Calcd for $C_{12}H_{44}P_4Re_2$: C, 21.04; H, 6.49. Found: C, 20.58; H, 6.56. Analogous results were found when $Re_2Br_4(PMe_3)_4$ was used as the starting complex and/or THF was used as the reaction solvent. However, a slightly lower yield of product is obtained in these latter reactions.

(ii) $Re_2H_8(PEt_3)_4$. The reaction between $Re_2Cl_4(PEt_3)_4$ (0.228 g, 0.231 mmol) and LAH (0.141 g, 3.714 mmol) in glyme (10 mL) was carried out as in part A(i). However, the procedure was slightly modified once the benzene extract was stripped down to give an orange oil. This was stirred vigorously with CH_3CN ($\simeq$10 mL) and then chilled as the solvent was slowly evaporated under vacuum. A microcrystalline solid began to form. The solid was quickly filtered off, washed sparingly with cold CH_3CN, and dried in vacuo; yield 0.020 g (10%). Anal. Calcd for $C_{24}H_{68}P_4Re_2$: C, 33.78; H, 8.05. Found: C, 33.56; H, 8.36. Note that on some occasions we found it difficult to isolate a solid product. However, a ^1H NMR spectrum (in C_6D_6) of the oily residue, obtained upon drying the benzene extract, showed the oil to contain only pure $Re_2H_8(PEt_3)_4$.

(iii) Re_2H_8(P-*n*-$Pr_3)_4$. A procedure similar to part A(i) was used to react Re_2Cl_4(P-*n*-$Pr_3)_4$ (0.240 g, 0.235 mmol) with LAH (0.127 g, 3.346 mmol) in glyme (10 mL). The mixture was stirred with gentle warming for a longer period of time (24–30 h), and variations in the workup of the oil obtained from the benzene filtrate were used. The oil was chilled with the use of an ice bath while cold CH_3CN (20–25 mL) was added with vigorous stirring. After this mixture was stirred for several hours at 0 °C, the orange solid that formed was filtered off, washed with CH_3CN, and vacuum dried; yield 0.059 g (28%). Anal. Calcd for $C_{36}H_{92}P_4Re_2$: C, 42.32; H, 9.10. Found: C, 43.18; H, 9.23. As was true for the PEt_3 derivative (see part A(ii)), a solid product was sometimes difficult to obtain. However, ^1H NMR spectroscopy (in C_6D_6) showed the oily residue, from the benzene extract, to be pure Re_2H_8(P-*n*-$Pr_3)_4$.

(iv) $Re_2H_8(PMe_2Ph)_4$. A sample of $Re_2Cl_4(PMe_2Ph)_4$ (0.502 g, 0.471 mmol) was combined with LAH (0.292 g, 7.692 mmol) in THF (20 mL) and reacted as in part A(i). The residue obtained following evaporation of the benzene extract was redissolved in THF (25 mL), and excess methanol ($\simeq$70 mL) was added. The mixture was chilled to obtain a red-orange solid. The solid was filtered off, washed with methanol, and dried in vacuo; yield 0.258 g (59%). Anal. Calcd for $C_{32}H_{52}P_4Re_2$: C, 41.19; H, 5.63. Found: C, 40.74; H, 5.86. This reaction can also be carried out with diethyl ether as the reaction solvent, but the product is obtained in lower yield ($\simeq$20%).

(v) $Re_2H_8(PEt_2Ph)_4$. A quantity of $Re_2Cl_4(PEt_2Ph)_4$ (0.170 g, 0.144 mmol) was combined with LAH (0.099 g, 2.608 mmol) in glyme (10 mL) and reacted as in part A(i). The oily residue that was obtained following evaporation of the benzene extract was stirred vigorously with CH_3CN (5–10 mL) at 0 °C. After 1–2 h, a red-orange solid had formed. This solid was filtered off, washed sparingly with CH_3CN, and dried under vacuum; yield 0.049 g (32%). The solid can be recrystallized from cold glyme/CH_3CN. Anal. Calcd for $C_{40}H_{68}P_4Re_2$: C, 45.96; H, 6.57. Found: C, 46.44; H, 6.73.

(vi) $Re_2H_8(PMePh_2)_4$. A procedure similar to part A(i) was used to react $Re_2Cl_4(PMePh_2)_4$ (0.129 g, 0.098 mmol) and LAH (0.060 g, 1.581 mmol) in glyme (10 mL). The residue obtained following workup of the benzene extract was redissolved in a small volume of THF; this solution was treated with an excess of methanol. The volume of the solution was reduced by slow evaporation to produce an orange solid. The solid was filtered off and vacuum dried; yield 0.023 g (20%). The identity of this product was established by ^1H NMR spectroscopy (in C_6D_6).[8]

(vii) $Re_2H_8(dppm)_2$. When $Re_2Cl_4(dppm)_2$ (0.209 g, 0.163 mmol) was reacted with LAH (0.109 g, 2.871 mmol) in THF (10 mL) as described in part A(i), a dark red residue was obtained following evaporation of the benzene extract. This residue was redissolved in a small volume of THF and an excess of methanol added. The rose-colored solid that formed was filtered off, washed with methanol, and vacuum dried; yield 0.065 g (35%). This product can be recrystallized from THF/*n*-pentane. Anal. Calcd for $C_{50}H_{52}P_4Re_2$: C, 52.25; H, 4.57. Found: C, 50.68; H, 4.85. The low carbon microanalysis is possibly attributable to the presence of water of crystallization. This reaction proceeds in the same manner, but in lower yield, when $Re_2Br_4(dppm)_2$ is used in place of $Re_2Cl_4(dppm)_2$.

(viii) $Re_2H_8(dppe)_2$. A quantity of $Re_2Cl_4(dppe)_2$ (0.237 g, 0.181 mmol) was reacted with LAH (0.136 g, 3.583 mmol) in THF (20 mL) as described in part A(i). However, the initial residue was *not* extracted with benzene. Instead, the residue was redissolved in THF and filtered. Then, the filtrate was reduced in volume, and excess methanol was added. The precipitate that formed was filtered off, washed with methanol, and dried under vacuum; yield 0.172 g (70%). Anal. Calcd for $C_{52}H_{56}P_4Re_2$: C, 53.04; H, 4.80. Found: C, 53.01; H, 4.87.

B. Oxidation Reactions of $Re_2H_8(PR_3)_4$. (i) Chemical Oxidations. Various attempts were made to chemically oxidize $Re_2H_8(PR_3)_4$ to the corresponding monocations, but in no instance were we able to isolate pure salts of the $[Re_2H_8(PR_3)_4]^+$ cations. For example, in our efforts to oxidize $Re_2H_8(PMe_3)_4$, we tried $(C_7H_7)PF_6$ in CH_2Cl_2 or CH_3CN, $(Ph_3C)PF_6$ in CH_2Cl_2, $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ in CH_2Cl_2 and $Os_2(O_2CCH_3)_4Cl_2$[17] in CH_2Cl_2 as oxidants. In all cases, whether low temperatures or room temperature were used, the reactions proceeded in a similar fashion. The solution rapidly turned purple and then proceeded to a brown color (within a few seconds) before isolation of a solid product could be accomplished. It is believed, on the basis of previous work,[18] that the purple color is attributable to the one-electron-oxidized species $[Re_2H_8(PMe_3)_4]^+$. However, once oxidized, this complex seems to be too unstable to maintain its integrity long enough to permit its isolation.

(ii) Electrochemical Oxidations. Bulk electrolyses were carried out on samples of several of the octahydride complexes, each of which exhibit a reversible oxidation at $E_{1/2} \simeq -0.3$ V and an irreversible process at $E_{p,a} \simeq +0.4$ V in their cyclic voltammograms. The course of these redox reactions was monitored by CV and ESR or electronic absorption spectroscopy. A sample of the octahydride complex was dissolved in a 0.1

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Table I. Crystallographic Data for $Re_2H_8(dppm)_2$

chemical formula	$Re_2P_4C_{50}H_{52}$	space group	$P2_1/n$ (No. 14)
		T, °C	−145
a, Å	12.962 (3)	λ, Å	Mo Kα (0.71073)
b, Å	12.002 (8)	ρ_{calcd}, g cm^{-3}	1.770
c, Å	14.979 (4)	μ(Mo Kα), cm^{-1}	58.67
β, deg	112.30 (2)	transm coeff	1.000–0.644
V, Å^3	2156 (3)	R[a]	0.048
Z	2	R_w[b]	0.057
fw	1149.27		

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

M TBAH/CH_2Cl_2 solution and an initial CV was recorded. From this solution a small aliquot was removed for use in ESR or electronic absorption spectroscopy. The remaining solution was then electrolyzed at a potential just positive (by ca. 0.2 V) of the reversible process. A color change from orange to purple ensued as this bulk oxidation proceeded. A CV of the electrolyzed solution was recorded and another aliquot removed for spectroscopic characterization. The purple solution was then rereduced by bulk electrolysis at a potential just negative (by ca. 0.2 V) of the reversible process. Once again, a CV was obtained and an aliquot removed for spectroscopic characterization.

C. Reactions Relating to the Mechanism of the Formation of the Octahydrides $Re_2H_8(PR_3)_4$. (i) Reaction of $Re_2H_8(PMe_3)_4$ with LAH. Procedure A(i) was used to react $Re_2H_8(PMe_3)_4$ (0.108 g, 0.158 mmol) with LAH (0.105 g, 2.766 mmol) in THF (10 mL). The reaction mixture was hydrolyzed after 2.5 days. A ^{1}H NMR spectrum (in C_6D_6) of the benzene extract (following its evaporation to dryness) exhibited a pentet at δ −6.9 and a triplet at δ −5.6. The pentet is due to unreacted octahydride, but the triplet arises from $ReH_7(PMe_3)_2$. Sublimation of the benzene residue at 50–70 °C in vacuo afforded a clean sample of white crystalline $ReH_7(PMe_3)_2$; yield 0.040 g (37%).

(ii) Reaction of a Mixture of $Re_2Cl_4(PMe_3)_4$ and $Re_2Cl_4(PMe_2Ph)_4$ with LAH. A mixture of $Re_2Cl_4(PMe_3)_4$ (0.104 g, 0.127 mmol) and $Re_2Cl_4(PMe_2Ph)_4$ (0.137 g, 0.128 mmol) was reacted with LAH (0.165 g, 4.347 mmol) in THF (15 mL) as in part A(i). A ^{1}H NMR spectrum (in C_6D_6) was taken of the residue obtained following evaporation of the benzene extract. Hydride resonances for $Re_2H_8(PMe_3)_4$ (δ −6.7, pentet), $Re_2H_8(PMe_2Ph)_4$ (δ −6.2, pentet), $ReH_7(PMe_3)_2$ (δ −5.5, triplet), and $ReH_7(PMe_2Ph)_2$ (δ −5.1, triplet) were observed. There was no resonance that we could attribute to the presence of any $Re_2H_8(PMe_3)_2(PMe_2Ph)_2$.

Preparation of Single Crystals of $Re_2H_8(dppm)_2$. Red crystals suitable for an X-ray crystallographic study were grown by diffusion of methanol into a solution of this complex in deoxygenated C_6D_6 contained in an NMR tube.

X-ray Crystallographic Procedures. The structure of $Re_2H_8(dppm)_2$ was determined by application of general procedures that are described more fully elsewhere.[19] The basic crystallographic parameters are listed in Table I. The cell constants are based on 25 reflections with $15.9 < \theta < 18.9°$. The intensities of three standard reflections were measured after every 5000 s of beam exposure during data collection. It was necessary to allow for an anisotropic decay correction through the use of the decay correction program CHORT (part of the Enraf-Nonius SDP package). All calculations were performed on a MicroVAX II computer using the Enraf-Nonius structure determination package.

The structure determination of this complex was carried out at low temperature. A single crystal of dimensions 0.14 × 0.11 × 0.06 mm was mounted on a glass fiber with vacuum grease and cooled to −145 °C in a cold stream of gaseous N_2 by using an Enraf-Nonius Type 524 temperature controller. The crystal was found to belong to the monoclinic space group $P2_1/n$ (standard space group $P2_1/c$, No. 14). The position of the crystallographically unique rhenium atom was determined from a three-dimensional Patterson map with the molecule residing on an inversion center. The remaining non-hydrogen atoms were located through alternating series of least-squares cycles and difference Fourier maps. One bridging hydride ligand atom was tentatively located in a difference Fourier search, which followed refinement of all non-hydrogen atoms.

In the refinement, an empirical absorption correction was applied.[20] The linear absorption coefficient was 58.67 cm^{-1}. No correction was made for extinction. The least-squares program minimized the function $\sum w(|F_o| - |F_c|)^2$, where w is the weighting factor defined as $w = 1/\sigma^2(F_o)$. The Re, P, and C atoms were refined anisotropically, and corrections for anomalous scattering were applied to these atoms.[21] Since the phenyl carbon atom C(211) assumed a nonpositive definite character when refined anisotropically, it was refined isotropically. In the final stages of refinement, the thermal parameter of the bridging hydride, H(1), took on a negative value. Consequently, this parameter was fixed at an arbitrary value for B of 0.5 Å^2. Positions for phenyl ring hydrogen atoms were calculated by assuming idealized geometry and a bond distance of 0.95 Å. For these hydrogen atoms we assumed that the value of B(H), i.e. the isotropic equivalent thermal parameter for the hydrogen atoms, was equal to $1.3B_{eqv}$(C) at the time of the inclusion of this parameter in the refinement procedure. While these phenyl ring hydrogens were used in the calculation of F_o, they were not included in the least-squares refinement. The final residuals were $R = 0.048$ and $R_w = 0.057$ for 6019

Table II. Positional Parameters and Equivalent Isotropic Displacement Parameters for $Re_2H_8(dppm)_2$ and Their Estimated Standard Deviations

atom	x	y	z	B,[a] Å^2
Re	−0.03373 (4)	0.10475 (4)	0.03152 (3)	1.321 (8)
P(1)	0.0318 (2)	0.1977 (3)	−0.0754 (2)	1.08 (6)
P(2)	0.0483 (2)	−0.0187 (3)	−0.1701 (2)	1.07 (6)
C(1)	−0.0029 (9)	0.1261 (9)	−0.1913 (7)	1.1 (2)
C(111)	0.1823 (9)	0.2197 (9)	−0.0387 (7)	1.2 (2)
C(112)	0.225 (1)	0.266 (1)	−0.1028 (8)	1.4 (2)
C(113)	0.340 (1)	0.281 (1)	−0.0757 (9)	1.8 (3)
C(114)	0.411 (1)	0.249 (1)	0.0152 (9)	2.6 (3)
C(115)	0.370 (1)	0.204 (1)	0.0788 (8)	1.9 (3)
C(116)	0.255 (1)	0.188 (1)	0.0525 (8)	1.6 (3)
C(121)	−0.025 (1)	0.337 (1)	−0.1176 (8)	1.4 (2)
C(122)	0.0391 (9)	0.433 (1)	−0.0863 (8)	1.6 (2)
C(123)	−0.007 (1)	0.536 (1)	−0.1170 (9)	2.3 (3)
C(124)	−0.119 (1)	0.547 (1)	−0.1796 (9)	2.2 (3)
C(125)	−0.181 (1)	0.451 (1)	−0.2104 (9)	2.2 (3)
C(126)	−0.137 (1)	0.348 (1)	−0.1783 (9)	1.8 (3)
C(211)	0.1859 (9)	−0.005 (1)	−0.1818 (8)	1.3 (2)*
C(212)	0.284 (1)	−0.041 (1)	−0.1078 (9)	2.0 (3)
C(213)	0.384 (1)	−0.030 (1)	−0.1190 (9)	2.6 (3)
C(214)	0.390 (1)	0.015 (1)	−0.2010 (9)	2.3 (3)
C(215)	0.295 (1)	0.052 (1)	−0.2723 (9)	2.5 (3)
C(216)	0.191 (1)	0.041 (1)	−0.2648 (8)	1.8 (3)
C(221)	−0.0351 (9)	−0.0813 (9)	−0.2882 (8)	1.3 (2)
C(222)	−0.044 (1)	−0.198 (1)	−0.2962 (8)	1.7 (3)
C(223)	−0.107 (1)	−0.248 (1)	−0.3819 (8)	1.9 (3)
C(224)	−0.164 (1)	−0.183 (1)	−0.4628 (9)	2.2 (3)
C(225)	−0.152 (1)	−0.068 (1)	−0.4569 (8)	2.0 (3)
C(226)	−0.089 (1)	−0.018 (1)	−0.3695 (8)	1.6 (3)
H(1)	0.39 (1)	0.51 (1)	0.440 (9)	0.5*

[a] Starred values are for atoms refined isotropically. Values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table III. Important Bond Distances (Å) and Bond Angles (deg) for $Re_2H_8(dppm)_2$[a]

	Distances		
Re–Re	2.9335 (9)	P(1)–C(111)	1.83 (1)
Re–P(1)	2.358 (3)	P(1)–C(121)	1.84 (1)
Re–P(2)	2.389 (3)	P(2)–C(1)	1.84 (1)
Re–H(1)	2.0 (1)	P(2)–C(211)	1.86 (1)
Re–H(1)	2.1 (1)	P(2)–C(221)	1.85 (1)
P(1)–C(1)	1.83 (1)		
	Angles		
Re–Re–P(1)	87.64 (8)	P(1)–Re–H(1)	82 (4)
Re–Re–P(2)	92.33 (7)	P(2)–Re–H(1)	96 (4)
Re–Re–H(1)	47 (4)	P(2)–Re–H(1)	88 (4)
Re–Re–H(1)	42 (4)	H(1)–Re–H(1)	88 (6)
P(1)–Re–P(2)	164.1 (1)	Re–P(1)–C(1)	113.5 (4)
P(1)–Re–H(1)	95 (4)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

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(19) Fanwick, P. E.; Harwood, W. S.; Walton, R. A. *Inorg. Chim. Acta* **1986**, *122*, 7.

(20) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found Crystallogr.* **1983**, *A39*, 158.

(21) (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.

Table IV. Cyclic Voltammetric Data and Certain Spectroscopic Properties for $Re_2H_8(PR_3)_4$

	CV half-wave potentials, V[a]			
PR_3 in complex	$E_{p,a}$	$E_{1/2}(ox)$[b]	IR ν(Re–H),[c] cm^{-1}	electronic abs λ,[d] nm (ϵ)
PMe_3	+0.34	−0.45 (100)	1935 ms	500 sh, 406 (2000), 361 (2500)
PEt_3	+0.34	−0.63 (120)	1990 sh, 1970 ms	500 sh, 410 (1800), 375 (2300)
P-*n*-Pr_3	+0.43	−0.60 (120)	1985 sh, 1966 m, 1942 ms	520 sh, 410 (1800), 375 (2200)
PMe_2Ph	+0.42	−0.34 (100)	1964 ms, 1938 s	500 sh, 440 sh, 375 (5800)
PEt_2Ph	+0.43	−0.42 (120)[e]	1974 ms, 1954 s	500 sh, 440 sh, 383 (6900)
$PMePh_2$	+0.62	−0.24 (120)	2000 sh, 1958 m	500 sh, 440 sh, 360 sh, 320 sh
PPh_3[f]	+0.60	−0.20 (120)[e]	2010 vs, 1990 vw[g]	470 sh, 380 sh, 352 (12 000)
$^1/_2$(dppm)	~+0.4	−0.11 (100)	1990 ms, br	485 (1000)
$^1/_2$(dppe)	+0.81	−0.02 (120)	1970 m	395 (5000), 325 sh

[a] Versus Ag/AgCl. Recorded on solutions in 0.1 M $TBAH/CH_2Cl_2$ by the use of a Pt-bead electrode. Data obtained at v = 200 mV s^{-1}. [b] Numbers in parentheses are ΔE_p (i.e. $E_{p,a} - E_{p,c}$) in mV. [c] Nujol mulls. [d] Recorded in CH_2Cl_2. Molar extinction coefficients (M^{-1} cm^{-1}) are given in parentheses. [e] Excellent agreement with literature data.[18] [f] Sample prepared by the method described in ref 6. [g] Data taken from ref 5.

data with $I > 3\sigma(I)$. The largest unassigned peak (3.03 e/Å^3) in the final Fourier difference map was situated very near the rhenium atom. This may be an artifact of a disorder associated with the terminal hydride ligands.

Further details concerning the data set, the structure solution, and the structure refinement may be obtained from P.E.F. Figure 1 shows an ORTEP representation of the structure with the atomic numbering scheme. Table II lists the atomic positional parameters and their errors, while Table III lists important intramolecular bond distances and angles. Tables giving full details of crystal data and data collection parameters (Table S1), positional parameters for the hydrogen atoms (Table S2), thermal parameters (Table S3), and complete bond distances and bond angles (Table S4 and S5, respectively) are available as supplementary material.

Physical Measurements. Infrared spectra (4000–400 cm^{-1}) were recorded as Nujol or halocarbon mulls with IBM Instruments IR/32 and Perkin-Elmer 1800 Fourier transform spectrometers. Electronic absorption spectra were recorded on IBM Instruments 9420 UV-visible (900–200 nm) and Hewlett-Packard HP8451A (820–190 nm) spectrophotometers. Electrochemical experiments were carried out by using a Bioanalytical Systems Inc. Model CV-1A instrument on dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the Ag/AgCl electrode at room temperature and are uncorrected for junction potentials. Under our experimental conditions, $E_{1/2}$ = +0.47 V vs Ag/AgCl for the ferrocenium/ferrocene couple, which was used as an internal standard. Bulk electrolyses were carried out with the use of a Pt-gauze working electrode and a Bioanalytical Systems Inc. Model SP-2 potentiostat. Conductivity measurements were performed on ca. 10^{-3} M acetone solutions by using an Industrial Instruments Inc. Model RC-16B2 conductivity bridge. ^{1}H NMR spectra were recorded on a Varian XL-200 spectrometer. Resonances were referenced internally to the residual protons in the incompletely deuteriated solvent. $^{31}P\{^1H\}$ spectra were recorded on a Varian XL-200 spectrometer operated at 80.98 MHz with an internal deuterium lock by using aqueous 85% H_3PO_4 as an external standard. X-Band ESR spectra of dichloromethane solutions were recorded at ca. −160 °C with the use of a Varian E-109 spectrometer. Mass spectral data were obtained through the Purdue University mass spectral service facility. The +CI mass spectrum of $ReH_7(PMe_3)_2$ was measured at 70 eV on a Finnegan 4000 mass spectrometer with the use of isobutane gas, a probe temperature of 150 °C, and a source temperature of 25 °C.

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

Results and Discussion

(a) Synthesis and Preliminary Characterization of $Re_2H_8(PR_3)_4$ (PR_3 = Monodentate Phosphine or Half of a Bidentate Phosphine). The new synthetic procedure we have developed for the synthesis of $Re_2H_8(PR_3)_4$ involves the use of compounds that already contain the desired $[(R_3P)_2ReRe(PR_3)_2]$ architecture, namely, the triply bonded dirhenium(II) phosphine complexes $Re_2Cl_4(PR_3)_4$.[11,12,14-16] The reactions between $Re_2Cl_4(PR_3)_4$ and $LiAlH_4$ (LAH) in glyme or THF at room temperature for 12–24 h, followed by hydrolysis of the reaction mixture with deoxygenated H_2O and workup (see the Experimental Section for details of the individual purification steps) gives the pure, orange octahydride complexes in yields of 30–70%. The only exception is $Re_2H_8(PEt_3)_4$, which was isolated as a pure solid in ca. 10% yield after separating it from a considerably quantity of $ReH_7(PEt_3)_2$ (see section d). This synthetic procedure represents the most general one available for complexes of this stoichiometry and has been used in the present work to prepare and characterize for the first time the derivatives where PR_3 = PEt_3, P-*n*-Pr_3, $Ph_2PCH_2PPh_2$ (dppm), and $Ph_2PCH_2CH_2PPh_2$ (dppe).

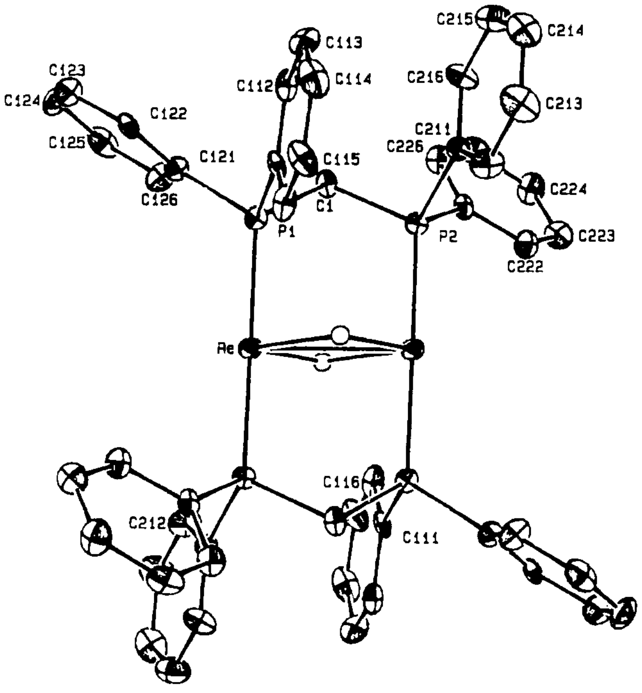

Figure 1. ORTEP representation of the structure of $Re_2H_8(dppm)_2$. The thermal ellipsoids are drawn at the 50% probability level. The probable positions of the two bridging hydride ligands H(1) are shown as circles of arbitrary radius.

The Nujol mull IR spectra of these complexes contain quite intense and well-defined ν(Re–H) modes near 1950 cm^{-1} (see Table IV). The PPh_3 derivative is the only exception, with ν(Re–H) bands at ≃2010 and ≃1990 cm^{-1} having been reported as being very weak.[5] The ν(Re–H) values for the PEt_2Ph and PMe_3 derivatives are in excellent agreement with previously reported results on these compounds, even though different preparative procedures were employed.[1,10]

Electronic absorption spectra were obtained for solutions of $Re_2H_8(PR_3)_4$ (PR_3 = monodentate phosphine) in deoxygenated CH_2Cl_2 (see Table IV). In all cases, two absorption bands were observed near 420 and 375 nm ($\epsilon > 1500$ M^{-1} cm^{-1}) and a shoulder of lower intensity was seen near 500 nm. The PEt_3 and P-*n*-Pr_3 derivatives were found to undergo oxidation very easily when these solutions were exposed (even briefly) to the air. The solutions turned purple in color due to the formation of $[Re_2H_8(PR_3)_4]^+$ (vide infra), and a new absorption band grew in at ca. 545 nm within 15–30 min. After approximately 1 h, however, these bands, as well as all other absorptions, had diminished in intensity as the solutions faded to a yellow color. The spectra of $Re_2H_8(dppm)_2$ and $Re_2H_8(dppe)_2$ differed from those of the monodentate phosphine derivatives in the range 300–900 nm, showing only bands at 395 nm (with a shoulder at ca. 375 nm) and 485 nm, respectively. These spectral differences can be taken as evidence for the existence of structural differences (vide infra).

The dirhenium octahydride complexes exhibit very similar electrochemical behavior as measured by the cyclic voltammetric (CV) technique. The CV's of solutions of these complexes in 0.1 M $TBAH/CH_2Cl_2$ show a reversible one-electron oxidation in the potential range −0.02 to −0.63 V and an irreversible oxidation between +0.34 and +0.81 V vs Ag/AgCl (Table IV). In several of the CV's, additional irreversible processes at more positive potentials (e.g., $E_{p,a}$ = +1.13 V for $Re_2H_8(PEt_3)_4$, +1.24 V for $Re_2H_8(P\text{-}n\text{-}Pr_3)_4$, +1.20 V for $Re_2H_8(PEt_2Ph)_4$, and $\simeq$+1.35 V for $Re_2H_8(dppe)_2$) can be attributed to the presence of chemical products formed following the second (irreversible) oxidation (labeled $E_{p,a}$ in Table IV). These data resemble closely that reported previously for $Re_2H_8(PPh_3)_4$ and $Re_2H_8(PEt_2Ph)_4$.[18,22] The trend in the $E_{1/2}$(ox) values correlates quite well with the basicity of the phosphine ($E_{1/2}$ for $PPh_3 > PPh_2R > PPhR_2 > PR_3$). In other words, oxidation is easiest with those complexes that contain the most basic phosphines. The CV of $Re_2H_8(dppm)_2$ merits further comment since the difference in potential between the $E_{1/2}$(ox) and $E_{p,a}$ values is much less than is the case for the other complexes listed in Table IV. This difference may signify a difference in electronic structure, a conclusion that is supported by the X-ray crystal structure of this dppm complex (vide supra). Note that the $E_{p,a}$ process at $\simeq$+0.4 V for $Re_2H_8(dppm)_2$ is rather poorly defined because of its proximity to a second, broad oxidation wave at $\simeq$+1.0 V, which very likely arises from a chemical product formed following the irreversible oxidation at +0.4 V.

While previous work established that $Re_2H_8(PPh_3)_4$ could be chemically oxidized by trityl hexafluorophosphate or tropylium hexafluorophosphate in CH_2Cl_2 to give $[Re_2H_8(PPh_3)_4]PF_6$, similar attempts to obtain the oxidized species with other derivatives ($PR_3 = PEt_2Ph$ or $PEtPh_2$) were unsuccessful.[18] Attempts to chemically oxidize many of the octahydrides reported in the present report also failed. A range of chemical oxidants were tried, and while they gave rise to the appropriate color changes, the resulting salts were very unstable and could not be isolated in a sufficiently pure state.

In the case of the monodentate phosphine complexes, the monocations can be generated in a controlled fashion when solutions of the complexes in 0.1 M $TBAH/CH_2Cl_2$ are subjected to bulk electrolyses at a potential just positive of the appropriate oxidation wave of the $E_{1/2}$(ox) couple (Table IV). These experiments were carried out in the case of $PR_3 = PMe_3$, $P\text{-}n\text{-}Pr_3$ and PMe_2Ph. The blue-purple solutions that resulted were shown to contain the paramagnetic $[Re_2H_8(PR_3)_4]^+$ species by three methods. (1) The CV's of the oxidized solutions were the same as those of their neutral precursors with the exception that the +/0 couple now corresponds to a reduction of the bulk species. The neutral complexes were regenerated through reduction of the oxidized solutions at a potential just negative of the $E_{p,c}$ component of the +/0 couple. (2) X-Band ESR spectra of CH_2Cl_2 glasses of the electrochemically generated dirhenium octahydride cations (at −160 °C) agreed well with those reported for the PPh_3, $PEtPh_2$, and PEt_2Ph derivatives.[18,22] The oxidized species were identified by a broad signal centered close to 3000 G with g values in the range 2.11–2.16. The signals are fairly symmetrical and show resolved rhenium hyperfine structure ($I = {}^5/_2$, $A_{Re} \simeq 120$ G). The spectrum of the $[Re_2H_8(P\text{-}n\text{-}Pr_3)_4]^+$ cation is shown in Figure 2. (3) The formation of these cations was followed by electronic absorption spectroscopy through the growth of a characteristic intense absorption band at ca. 550 nm. For example, spectral measurements in the case of $[Re_2H_8(PMe_3)_4]^+$ and $[Re_2H_8(P\text{-}n\text{-}Pr_3)_4]^+$ (in 0.1 M $TBAH/CH_2Cl_2$) showed this band to be at 540 and 550 nm, respectively, with ϵ values of $\gtrsim$2000 M^{-1} cm^{-1}. For the sake of comparison, we also recorded the spectrum of $[Re_2H_8(PPh_3)_4]^+$ under these same conditions; its spectrum shows a band at 575 nm ($\epsilon \simeq 2500$).

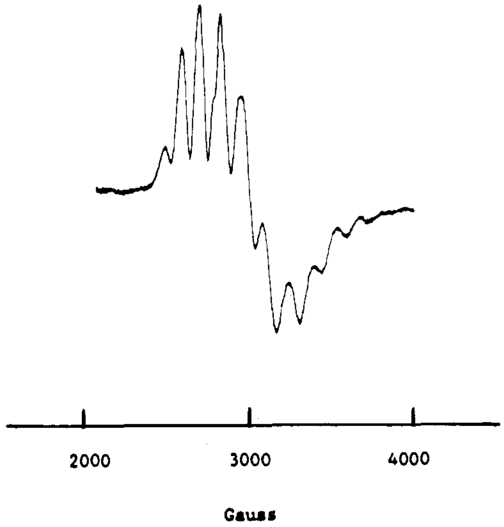

Figure 2. X-Band ESR spectrum of a solution of the electrochemically generated $[Re_2H_8(P\text{-}n\text{-}Pr_3)_4]^+$ cation in 0.1 M $TBAH/CH_2Cl_2$ at −160 °C.

Table V. NMR Spectral Properties for $Re_2H_8(PR_3)_4$

PR_3 in complex	^1H NMR (Re-H),[a] δ		$^{31}P\{^1H\}$ NMR,[b] δ	
	C_6D_6	CD_2Cl_2	C_6D_6	CD_2Cl_2
PMe_3	−6.68 (10.0)	−7.40 (9.5)	−25.9[g]	−25.9
PEt_3	−7.35 (10.0)		+24.2	
$P\text{-}n\text{-}Pr_3$	−7.31 (10.0)	−8.03 s, br[c]	+15.0	+17.9
PMe_2Ph	−6.22 (9.5)	−6.89 (9.0)	−8.11	
PEt_2Ph	−6.56 (9.5)	−7.17 (9.0)	+26.7	
$PMePh_2$	−5.8[d]	−6.41 (8.5)		+13.0
PPh_3	−5.01 (8.0)[e]	−5.6 (9.5)[f]	+42.3	
$^1/_2$(dppm)	−5.46 (10.5)	−6.20 (11.0)	+35.0	+34.5
$^1/_2$(dpp)	−6.01 (9.5)	−6.62 (9.5)	+53.1	+50.6

[a] All spectra appear as a binomial pentet unless otherwise indicated. $^2J_{PH}$ coupling constants (in Hz) given in parentheses (to ±0.5 Hz). [b] Spectra were recorded with aqueous 85% H_3PO_4 as an external reference. All spectra appear as singlets. [c] Resonance appears as a broad singlet. [d] Poorly resolved pentet; spectrum recorded at 90 MHz. [e] Data from ref 8. [f] Data from ref 6. [g] Value of δ −27.2 reported in ref 10.

Bulk electrolyses of solutions of $Re_2H_8(dppm)_2$ and $Re_2H_8(dppe)_2$ in 0.1 M $TBAH/CH_2Cl_2$ give results different from the above. Both solutions turned green and neither gave species that appeared to be ESR active (spectra recorded at −160 °C). CV measurements on solutions of the dppe complex revealed that its structural integrity had not been maintained. A new chemical species had been formed upon electrolysis that showed well-defined redox processes at $E_{1/2}$ = +0.75 V and $E_{1/2}$ = −0.74 V vs Ag/AgCl. Further studies are under way to examine in more detail the changes that follow oxidation of the dppm and dppe derivatives.

(b) NMR Spectral Properties. The ^1H NMR spectral properties of the PMe_3, PMe_2Ph, PEt_2Ph, and $PMePh_2$ derivatives (recorded in C_6D_6 or CD_2Cl_2) agree well with literature data.[1,2,7,8,10] The important features of these spectra, along with those for the previously unreported PEt_3, $P\text{-}n\text{-}Pr_3$, dppm, and dppe complexes, are presented in Table V. At room temperature, the Re–H resonance appears as a binomial pentet. This arises from the eight hydride ligands being coupled to four equivalent phosphorus nuclei. The J_{PH} coupling constants are in the range 8–11 Hz. At room temperature, all of the hydride ligands are moving rapidly between bridging and terminal sites; therefore, they appear equivalent on the NMR time scale. However, when these solutions are cooled to −70 °C or thereabouts, the symmetrical pentet broadens with loss of resolution. While we did not observe limiting chemical shift values at low temperature that could be assigned to inequivalent terminal and bridging hydride ligands, coalescence was achieved at ca. −80 °C for $Re_2H_8(dppe)_2$.

The $^{31}P\{^1H\}$ NMR spectra (in C_6D_6 or CD_2Cl_2) show a singlet for each complex (Table V). Integrations of the ^1H NMR spectra

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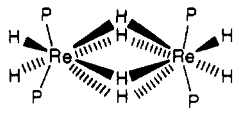
(22) Allison, J. D.; Cameron, C. J.; Wild, R. E.; Walton, R. A. *J. Organomet. Chem.* **1981**, *218*, C62.

were consistent with the presence of approximately eight hydride ligands. However, in order to determine *exactly* how many hydride ligands were present in these complexes, two ^{31}P NMR techniques were utilized. For $Re_2H_8(PMe_3)_4$, the easiest way to determine the number of hydrides was to record a ^{31}P NMR spectrum with selective decoupling of the methyl protons. A nonet with J_{PH} = 10.0 Hz was reported by Lyons and Wilkinson[10] and confirmed herein (J_{PH} = 9.6 Hz). This nine-line pattern signifies that the equivalent phosphorus nuclei are being split by eight equivalent hydride ligands. A second technique, which proved to be an effective method, was selective 2DJ NMR spectroscopy. This technique gave spectra consisting of binomial nonets centered at δ +34.5 (J_{PH} = 11.9 Hz) and δ +50.6 (J_{PH} = 8.8 Hz), respectively, for $Re_2H_8(dppm)_2$ and $Re_2H_8(dppe)_2$. The ^{31}P 2DJ NMR spectrum of $Re_2H_8(dppm)_2$ is available as supplementary material (Figure S1). These results confirm the presence of eight hydride ligands in these complexes.

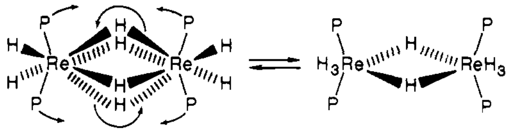
(c) X-ray Crystal Structure Determination on $Re_2H_8(dppm)_2$ and General Structural Considerations. The close similarities in spectroscopic and electrochemical properties for the monodentate phosphine complexes of the type $Re_2H_8(PR_3)_4$ imply that at least in solution they possess very similar structures. Since a neutron diffraction analysis of $Re_2H_8(PEt_2Ph)_4$ has shown it to have structure I in the solid state (i.e., $(PhEt_2P)_2H_2Re(\mu\text{-}H)_4ReH_2(PEt_2Ph)_2$),[2] it is reasonable to expect similar structures for the other complexes where PR_3 represents a *monodentate* phosphine ligand. Note that in this structure, the two terminal ReH_2P_2 units are eclipsed with respect to one another while the four bridging hydride ligands assume a staggered disposition relative to these terminal units. Preliminary X-ray structure determinations have shown that the Re_2P_4 skeletons in $Re_2H_8(PMe_3)_4$[10] and $Re_2H_8(PPh_3)_4$[23] are planar and similar to that in $Re_2H_8(PEt_2Ph)_4$, with Re–Re distances of 2.53 Å and P–Re–P angles of ca. 105°. Interestingly, very recent structural work by Cotton and Luck[24] has demonstrated that there are at least two structural forms of $Re_2H_8(PPh_3)_4$ in the solid state, one that is structurally similar to that characterized by Caulton et al.[23] and a second form in which the pair of $Re(PPh_3)_2$ units have a staggered arrangement to one another. Accordingly, while we are confident that the dirhenium octahydride complexes that contain monodentate phosphines bear a very close structural relationship to one another in *solution*, the same may not necessarily be true in the *solid state*.


I

A comparison of the spectroscopic and electrochemical properties of $Re_2H_8(dppe)_2$ and $Re_2H_8(dppm)_2$ with those of the other $Re_2H_8(PR_3)_4$ complexes (vide supra) suggests that these two complexes have structures somewhat different from that depicted in I. The complex $Re_2H_8(dppe)_2$ almost certainly contains chelating dppe ligands as evidenced by its $^{31}P\{^1H\}$ NMR spectrum (C_6D_6), which shows a singlet at δ +53.1 (Table V), a chemical shift that is characteristic of a five-membered ring formed by chelating phosphines bound to rhenium.[25] Thus, the formation of $Re_2H_8(dppe)_2$ from β-$Re_2Cl_4(dppe)_2$ involves a switch in the bonding of the two dppe ligands from an intramolecular bridging mode in β-$Re_2Cl_4(dppe)_2$[26] to a chelating mode in the octahydride complex. Unfortunately, we have not as yet been able to obtain suitable single crystals of $Re_2H_8(dppe)_2$ to confirm that this is the structure in the solid state.

The conversion of $Re_2Cl_4(\mu\text{-dppm})_2$[16,27] into $Re_2H_8(dppm)_2$ upon its reaction with LAH occurs with retention of the intramolecularly bridging dppm ligands as shown by a crystal structure determination of this complex (Figure 1). Important bond distances and angles are given in Table III. The molecules have crystallographically imposed $\bar{1}$ symmetry. The most important features of this structure are (1) a Re–Re distance (2.933 (1) Å) that is ca. 0.4 Å longer than in $Re_2H_8(PEt_2Ph)_4$,[2] $Re_2H_8(PMe_3)_4$,[10] and $Re_2H_8(PPh_3)_4$,[23] and (2) a P–Re–P angle (164.1 (1)°) that is much larger than the corresponding angles of ca. 103–105°, which characterize the derivatives containing monodentate phosphines.[2,10,23] Although we were unable to locate the terminal hydride ligands in this structure determination, we found evidence for a bridging hydride ligand in a difference Fourier map. Isotropic refinement on this assumption led to Re–H(1) distances of 2.0 (1) and 2.1 (1) Å. While these distances are much longer than the Re–H bridging bonds in $Re_2H_8(PEt_2Ph)_4$,[2] the Re–H–Re bridges in $Re_2H_8(dppm)_2$ are of course spanning a much longer Re–Re bond. While we cannot be certain that we have correctly located this pair of hydride ligands, nonetheless, we are confident that our overall structural conclusions are correct based upon the other structural features of this complex and the striking differences that exist between it and $Re_2(\mu\text{-}H)_4H_4(PEt_2Ph)_4$.

The structure of $Re_2H_8(dppm)_2$ can be considered to represent a distortion from $Re_2(\mu\text{-}H)_4H_4(PR_3)_4$ in which an opening up of the P–Re–P angles (constrained here to do so by the nature of the bridging dppm ligands) and a concomitant lengthening of the Re–Re bond are accompanied by a conversion of two of the bridging Re–H–Re units to terminal Re–H bonds. This "concertina-like" motion (as represented in eq 1) is probably a low-energy process and could be the origin of the fluxionality of this class of molecule as a whole, although other mechanisms are no doubt possible. It seems reasonable to conclude that the long Re–Re distance, coupled with the observed diamagnetism of the dppm complex, accords with the presence of a Re–Re single bond and, most likely, only a 16-electron count for the Re centers. Formally, at least, the dramatic Re–Re bond shortening that accompanies conversion to the $Re(\mu\text{-}H)_4Re$ structure is consistent with an 18-electron count and a Re≡Re bond. An alternative description of the latter system in terms of a 16-electron count and a Re—Re single bond enhanced by four strong Re–H–Re bridging units is also reasonable.


(1)

(d) Reaction Pathways. The conversion of $Re_2Cl_4(PR_3)_4$ to $Re_2H_8(PR_3)_4$ most likely proceeds through the intermediacy of aluminohydride complexes,[28] in which the "oxidation" of the Re_2^{4+} core to Re_2^{8+} can be considered to arise through a sequence of hydride anion transfers and concomitant protonation steps in the hydrolysis process during the workup procedure. While the mechanistic details involved in these reactions were not established, we carried out several additional experiments that served to shed some light on the most likely reaction pathway. Specifically, does the conversion of $Re_2Cl_4(PR_3)_4$ to $Re_2H_8(PR_3)_4$ occur by a sequence of reactions in which the dirhenium unit is maintained throughout, or do these reactions require the formation of the corresponding monomeric heptahydride $ReH_7(PR_3)_2$, which then loses H_2 thermally and dimerizes to give $Re_2H_8(PR_3)_4$? The latter pathway is a reasonable possibility since certain $ReH_7(PR_3)_2$ complexes (PR_3 = PPh_3, PEt_2Ph, PMe_2Ph) are known to convert in this fashion upon thermolysis.[1,3] However, that this is not always the case is demonstrated by the comparative thermal stability of $ReH_7[P(C_6H_{11})_3]_2$.[4]

First, we note that the thermolysis of $ReH_7(PR_3)_2$ intermediates to give significant quantities of $Re_2H_8(PR_3)_4$ is not favored by

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[23] Caulton, K. G.; Sartain, W. J.; Folting, K.; Streib, W. E. Unpublished results. We thank Dr. W. J. Sartain for making this information available to us and Professor K. G. Caulton for permission to quote this result.

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the relatively mild reaction conditions that we used. To support this contention, we reacted a mixture containing equimolar amounts of $Re_2Cl_4(PMe_3)_4$ and $Re_2Cl_4(PMe_2Ph)_4$ with LAH under the usual reaction conditions in the expectation that if the dimetal unit is maintained throughout, we would obtain only a mixture of $Re_2H_8(PMe_3)_4$ and $Re_2H_8(PMe_2Ph)_4$ but no $Re_2H_8(PMe_3)_2(PMe_2Ph)_2$. The mixed phosphine complex is a possible product if mononuclear intermediates are involved. ^1H NMR spectroscopy showed the product to be a mixture of the single phosphine complexes, and there was no evidence for significant amounts of the mixed phosphine derivative. However, considerable quantities of mononuclear $ReH_7(PMe_3)_2$ (δ −5.48, triplet, J_{PH} = 21 Hz) and $ReH_7(PMe_2Ph)_2$ (δ −5.09, triplet, J_{PH} = 20 Hz) were present.

The preceding observation suggested to us that rather than $ReH_7(PR_3)_2$ actually being an intermediate in the formation of $Re_2H_8(PR_3)_4$, this mononuclear complex was in fact a product of the reaction between the dirhenium octahydride complex and LAH. To confirm this, we reacted pure $Re_2H_8(PMe_3)_4$ with an excess of LAH under the usual (mild) reaction conditions and obtained white crystalline $ReH_7(PMe_3)_2$ in fairly good yield (ca. 40%). This observation also accords with the formation of appreciable quantities of $ReH_7(PEt_3)_2$[29] during the synthesis of $Re_2H_8(PEt_3)_4$. In this particular system, it seems that $Re_2H_8(PEt_3)_4$ is particularly susceptible to further reaction with LAH to give $ReH_7(PEt_3)_2$.

The heptahydride complex $ReH_7(PMe_3)_2$, which we prepared from the reaction of $Re_2H_8(PMe_3)_4$ with LAH, was first synthesized by Lyons and Wilkinson[10] through the interaction of $Re(NPh)Cl_3(PMe_3)_2$ with LAH in diethyl ether followed by cooling to −78 °C and treatment with methanol. Workup gave the aniline adduct $ReH_7(PMe_3)_2 \cdot PhNH_2$, and this afforded $ReH_7(PMe_3)_2$ upon sublimation. We have confirmed the volatility of $ReH_7(PMe_3)_2$ by using a sublimation procedure to separate it from the less volatile $Re_2H_8(PMe_3)_4$ in a static vacuum. The crystalline product so obtained had a ^1H NMR spectrum (recorded in C_6D_6) that agreed closely with that reported by Lyons and Wilkinson,[10] with the Re–*H* resonance at δ −5.5 (triplet, J_{PH} = 21) and the P–CH_3 resonance at δ +1.5 (pseudotriplet). The ν(Re–H) modes in the IR spectrum of this complex (Nujol mull) are present at 1962 (m), 1902 (s), and 1872 (s) cm^{-1}, frequencies that compare quite closely with literature values[10] of 1975 (s), 1900 (s) and 1860 (s) cm^{-1}. Interestingly, we see very clear IR spectral evidence for water of crystallization in this complex with ν(OH) at 3410 (m, br) and δ(OH) at 1655 (w, br) cm^{-1}. This is further supported by the +CI mass spectrum, in which high mass peaks at *m/e* 361 and 363 (17 and 27% relative abundance, respectively) correspond to $(M-H)^+$, where M = $ReH_7(PMe_3)_2 \cdot H_2O$; a very weak peak at *m/e* 364 (1% abundance) may be due to M^+. Under these same experimental conditions the base peak is at *m/e* 345 (100% abundance) with associated peaks at *m/e* 347, 343, and 341 (24%, 60%, and 7% abundance, respectively). The peak at *m/e* 345 is assigned to the ion $(M-H_2O-H)^+$, i.e. "$[ReH_6(PMe_3)_2]^+$." With time, the "hydrate" peaks at *m/e* 363 and 361 decrease in intensity as water is lost under the high-vacuum conditions in the mass spectrometer; during this same period, the cluster of peaks centered at *m/e* 345 change very little.

The preceding mass spectral data not only demonstrate the existence of $ReH_7(PMe_3)_2$ as its "hydrate", but also confirm the considerable stability of this complex toward thermal loss of H_2. This in turn indicates that in the gas phase, and probably in the solid state also, $ReH_7(PMe_3)_2$ is an authentic heptahydride and not the dihydrogen adduct $Re(\eta^2-H_2)H_5(PMe_3)_2$.[30,31] It resembles $ReH_7[P(C_6H_{11})_3]_2$ in its stability toward H_2 loss,[4] and in the *solid state*, its structure may well be closely akin to that of the structurally characterized complex $ReH_7(dppe)$.[32] However, this is not necessarily reflective of the structure in solution since we find that the cyclic voltammograms of solutions of this complex in 0.1 M TBAH/CH_2Cl_2 exhibit a well-defined oxidation process at $E_{p,a}$ = +1.31 V vs Ag/AgCl. This behavior is very similar to that shown by other complexes of the type $ReH_7(PR_3)_2$ in this same solvent system[33] and suggests that in *solution* the formulation $Re(\eta^2-H_2)H_5(PMe_3)_2$ may well be an accurate description. Therefore, the properties of $ReH_7(PMe_3)_2$ provide good evidence for a structure change upon changing from the gas phase (and solid state) to solution.

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Supplementary Material Available: Tables giving full details of crystal data and data collection parameters (Table S1), positional parameters for the phenyl ring hydrogen atoms (Table S2), thermal parameters (Table S3), and bond distances and bond angles (Tables S4 and S5, respectively) and a figure (Figure S1) showing the ^{31}P 2DJ NMR spectrum of $Re_2H_8(dppm)_2$ (9 pages); a table of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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(29) The identity of $ReH_7(PEt_3)_2$ was based upon its ^1H NMR spectral properties in C_6D_6 (Re–*H*, δ −6.4, triplet, $J_{PH} \simeq$ 20 Hz), which agree closely with data available elsewhere (see: Green, M. A. Ph.D. Thesis, Indiana University, 1982).

(30) Such a possibility is based upon the suggestion of Hamilton and Crabtree[31] that $ReH_7(PPh_3)_2$ and $ReH_7(dppe)$ can be formulated as $Re(\eta^2-H_2)H_5(PPh_3)_2$ and $Re(\eta^2-H_2)H_5(dppe)$ on the basis of T_1 NMR measurements in toluene and dichloromethane.

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