Dirhenium Polyhydrides That Contain Bidentate Chelating and/or Bridging Phosphine Ligands

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The dirhenium octahydride complex $Re_2H_8(dppe)_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$) reacts with 2 equiv of dppe in methanol to give $Re_2H_4(dppe)_3$. This complex displays ^1H and $^{31}P\{^1H\}$ NMR spectra which are consistent with its possessing the unsymmetrical structure $(dppe)_2Re(\mu\text{-}H)_2ReH_2(dppe)$, in which all three dppe ligands are chelating. The conversion of $Re_2H_4(dppe)_3$ to its conjugate acid $[Re_2H_5(dppe)_3]BF_4$ was accomplished upon its treatment with $HBF_4{\cdot}Et_2O$ in CH_2Cl_2. The structure of the dirhenium cation $[Re_2H_5(dppe)_3]^+$ was established by NMR spectroscopy and a crystal structure determination on the salt $[Re_2H_5(dppe)_3]ReO_4$ (**1**), which was isolated, along with $[ReO_2(dppe)_2]ReO_4$ (**2**), during an unsuccessful attempt to grow single crystals of the octahydride $Re_2H_8(dppe)_2$. Crystal data for **1** (+21 °C): monoclinic space group $P2_1/n$ (No. 14), a = 12.177 (1) Å, b = 23.152 (2) Å, c = 26.843 (4) Å, β = 100.32 (1)°, V = 7445 (3) Å^3, and Z = 4. The structure, which was refined to R = 0.048 (R_w = 0.060) for 5923 data with $I > 3.0\sigma(I)$, reveals the presence of one intramolecular bridging and two inequivalent chelating dppe ligands, in accord with the structure representation $[(dppe)HRe(\mu\text{-}H)_3(\mu\text{-}dppe)ReH(dppe)]^+$. The Re–Re bond length is 2.576 (1) Å. Crystal data for **2** (+21 °C): monoclinic space group $P2_1/n$ (No. 14), a = 9.805 (2) Å, b = 14.500 (3) Å, c = 17.572 (4) Å, β = 92.89 (2)°, V = 2495 (2) Å^3, and Z = 2. The structure was refined to R = 0.067 (R_w = 0.086) for 2790 data with $I > 3.0\sigma(I)$; it contains the centrosymmetric *trans*-$[ReO_2(dppe)_2]^+$ cation. Several other complexes that are related to $Re_2H_4(dppe)_3$ and $[Re_2H_5(dppe)_3]^+$ have been isolated in which mixed-phosphine ligand sets are present. These are of compositions $Re_2H_4(dppe)_2(dppm)$, $[Re_2H_5(dppe)_2(dppm)]BF_4$, $Re_2H_4(PMe_3)_4(dppe)$, $[Re_2H_5(PMe_3)_4(dppe)]X$ (X^- = BF_4^-, PF_6^-), and $[Re_2H_5(PMe_3)_4(dppm)]PF_6$, where dppm = $Ph_2PCH_2PPh_2$. The mixed dppe–dppm complexes are believed to have the structures $(dppe)Re(\mu\text{-}H)_3(\mu\text{-}dppm)ReH(dppe)$ and $[(dppe)HRe(\mu\text{-}H)_3(\mu\text{-}dppm)ReH(dppe)]^+$, respectively, on the basis of an analysis of their ^1H and $^{31}P\{^1H\}$ NMR spectra. The structures of the mixed PMe_3–dppe and PMe_3–dppm complexes are less certain. The complex cation $[Re_2H_5(dmpm)_3]^+$ (dmpm = $Me_2PCH_2PMe_2$), which has been prepared by two different procedures, is quite different structurally from $[Re_2H_5(dppe)_2(LL)]^+$ (LL = dppe, dppm). The reaction of $Re_2Cl_4(\mu\text{-}dmpm)_3$ with $LiAlH_4$ in THF, followed by treatment of the reaction product with KPF_6 in water, affords the complex $[Re_2H_5(dmpm)_3]PF_6$ (**3**), while the analogous BF_4^- salt is prepared from the reaction between $Re_2H_8(dmpm)_2$, dmpm, and $HBF_4{\cdot}Et_2O$. Crystal data for **3** at −100 °C: monoclinic space group $P2_1/n$ (No. 14), a = 9.288 (1) Å, b = 24.515 (3) Å, c = 13.761 (3) Å, β = 93.23 (1)°, V = 3128 (1) Å^3, and Z = 4. The structure was refined to R = 0.030 (R_w = 0.039) for 4476 data with $I > 3\sigma(I)$. The cation has the solid-state structure $[H_2Re(\mu\text{-}H)(\mu\text{-}dmpm)_3ReH_2]^+$, in which the only Re–Re interaction is through a 3-center, 2-electron bond; the Re–Re distance is 3.5150 (4) Å. This molecule has a degree of electronic unsaturation remarkable for a polyhydride complex of a heavier transition element.

Introduction

Dirhenium octahydride complexes of the type $Re_2H_8(PR_3)_4$, where PR_3 represents a monodentate phosphine ligand, have attracted interest recently in several series of studies aimed at developing useful synthetic strategies, elucidating the structures of these compounds, and exploring their chemical reactivities.[1-20] However, there are only two examples of complexes in which bidentate phosphines are present, namely, $Re_2H_8(\mu\text{-}dppm)_2$ (dppm = $Ph_2PCH_2PPh_2$), in which the dppm ligands bridge the two metal centers, and $Re_2H_8(dppe)_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$), wherein which each of the dppe ligands chelates a metal center.[6,7] We now describe the isolation of a third such example, $Re_2H_8(\mu\text{-}dmpm)_2$ (dmpm = $Me_2PCH_2PMe_2$), as well as the results of studies that examine the chemical reactivity of these three compounds. The crystal structures of three chemical products are reported, viz., $[Re_2H_5(dppe)_3]ReO_4$, $[Re_2H_5(dmpm)_3]PF_6$, and $[ReO_2(dppe)_2]ReO_4$. A few of these results have been described previously in communication form.[21]

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(1) Chatt, J.; Coffey, R. S. *J. Chem. Soc. A* **1969**, 1963.
(2) (a) Green, M. A.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 695. (b) Roberts, D. A.; Geoffroy, G. L. *J. Organomet. Chem.* **1981**, *214*, 221.
(3) Brant, P.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 2674.
(4) Bruno, J. W.; Caulton, K. G. *J. Organomet. Chem.* **1986**, *315*, C13.
(5) Lyons, D.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1985**, 587.
(6) Fanwick, P. E.; Root, D. R.; Walton, R. A. *Inorg. Chem.* **1989**, *28*, 395.
(7) Fanwick, P. E.; Root, D. R.; Walton, R. A. *Inorg. Chem.* **1989**, *28*, 3203.
(8) Costello, M. T.; Moehring, G. A.; Walton, R. A. *Inorg. Chem.* **1990**, *29*, 1578.
(9) Bau, R.; Carroll, W. E.; Teller, R. G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 3872.
(10) Cotton, F. A.; Luck, R. L. *Inorg. Chem.* **1989**, *28*, 4522.
(11) Cotton, F. A.; Luck, R. L.; Root, D. R.; Walton, R. A. *Inorg. Chem.* **1990**, *29*, 43.
(12) (a) Allison, J. D.; Walton, R. A. *J. Chem. Soc., Chem. Commun.* **1983**, 401. (b) Allison, J. D.; Walton, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 163.
(13) Moehring, G. A.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1987**, *26*, 1861.
(14) Root, D. R.; Meyer, K. E.; Walton, R. A. *Inorg. Chem.* **1989**, *28*, 2503.
(15) Costello, M. T.; Fanwick, P. E.; Meyer, K. E.; Walton, R. A. *Inorg. Chem.* **1990**, *29*, 4437.
(16) Allison, J. D.; Cotton, F. A.; Powell, G. L.; Walton, R. A. *Inorg. Chem.* **1984**, *23*, 159.
(17) Rhodes, L. F.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1983**, *105*, 5137.
(18) Mueting, A. M.; Bos, W.; Alexander, B. D.; Boyle, P. D.; Casalnuovo, J. A.; Balaban, S.; Ito, L. N.; Johnson, S. M.; Pignolet, L. H. *New J. Chem.* **1988**, *12*, 505.
(19) Westerberg, D. E.; Sutherland, B. R.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1988**, *110*, 1642.
(20) Green, M. A.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1982**, *104*, 2319.
(21) (a) Fanwick, P. E.; Root, D. R.; Walton, R. A. *Inorg. Chem.* **1989**, *28*, 2239. (b) Meyer, K. E.; Fanwick, P. E.; Walton, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 8586.

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Experimental Section

Starting Materials. The dirhenium octahydride complexes $Re_2H_8(\mu\text{-dppm})_2$, $Re_2H_8(dppe)_2$, and $Re_2H_8(PMe_3)_4$ were prepared as described previously.[7] The dmpm complexes $Re_2Cl_4(\mu\text{-dmpm})_3$[22] and $Re_2(\mu\text{-}O_2CCH_3)Cl_4(\mu\text{-dmpm})_2$[23] were also obtained from published procedures. Trimethylphosphine and dmpm were purchased from Quantum Design, Inc., and Strem Chemicals, while dppe and dppm were obtained from Pressure Chemical Co. These ligands were used as received. The remaining reagents and solvents were obtained from commercial sources and used without further purification. Solvents were deoxygenated prior to use.

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

A. Synthesis of $Re_2H_8(\mu\text{-dmpm})_2$. A quantity of $Re_2(O_2CCH_3)Cl_4(dmpm)_2$ (0.248 g, 0.293 mmol) was mixed with 0.23 g of $LiAlH_4$ (6.1 mmol) and 15 mL of THF. The green reaction mixture was stirred at room temperature for 17 h and then cooled to −78 °C. The solution was hydrolyzed with a mixture of 5 mL of H_2O and 15 mL of THF that was added dropwise to the reaction flask. As the mixture warmed to room temperature, the color of the solution changed to brown, and after 2 h the reaction mixture was filtered by use of a cannula. The filtrate was collected and evaporated to dryness under vacuum. A minimum volume of benzene was added to extract the red-brown product, and this solution was filtered as before. The benzene solvent was removed under reduced pressure. The product, which appears red in solution, was isolated as a green solid and dried under vacuum; yield 0.065 g (34%). Anal. Calcd for $C_{10}H_{36}P_4Re_2$: C, 18.40; H, 5.57. Found: C, 18.59; H, 6.34.

B. Reactions of $Re_2H_8(dppe)_2$. (i) Formation of $Re_2H_4(dppe)_3$. A mixture of $Re_2H_8(dppe)_2$ (0.19 g, 0.16 mmol) and dppe (0.14 g, 0.36 mmol) was placed in a round-bottom flask equipped with a stir bar and N_2 inlet. The system was purged with gaseous N_2, 15 mL of THF was added, and the mixture was stirred at room temperature for 17 h. The orange solution was treated with methanol (30 mL), and the volume was reduced by evaporation to give a red-brown solid. Filtration was carried out under N_2 by use of a cannula, and the product was washed sparingly with methanol and diethyl ether; yield 0.20 g (78%). Anal. Calcd for $C_{78}H_{76}P_6Re_2$: C, 59.60; H, 4.88. Found: C, 59.21; H, 5.21.

This same product was isolated in 67% yield when benzene was used in place of THF as the reaction solvent.

(ii) Formation of $Re_2H_4(dppe)_2(dppm)$. With the use of a procedure similar to that in section B(i), 0.100 g of $Re_2H_8(dppe)_2$ (0.085 mmol) and 0.072 g of dppm (0.19 mmol) were reacted together in THF for 24 h. Following completion of the reaction, the volume of the solvent was reduced to <2 mL under a stream of gaseous N_2. An excess of methanol was added to the concentrated solution to initiate precipitation of the brown product, and the product was filtered off and washed with methanol and diethyl ether; yield 0.062 g (47%). Anal. Calcd for $C_{77}H_{74}P_6Re_2$: C, 59.37; H, 4.80. Found: C, 59.13; H, 5.05.

C. Reaction of $Re_2H_8(PMe_3)_4$ with dppe. Formation of $Re_2H_4(PMe_3)_4(dppe)$. With the use of a procedure similar to that in section B(i), a mixture of $Re_2H_8(PMe_3)_4$ (0.040 g, 0.058 mmol) and dppe (0.023 g, 0.058 mmol) in 5 mL of THF was stirred at room temperature for 17 h. The bright orange solution was then evaporated to ca. 1 mL under a stream of gaseous N_2, and ethanol was added to precipitate the red-orange product. Filtration was carried out quickly to avoid oxidation of the product; yield 0.015 g (24%). Anal. Calcd for $C_{38}H_{72}O_4P_6Re_2$ (i.e. $Re_2H_4(PMe_3)_4(dppe)\cdot 4H_2O$): C, 39.64; H, 6.32. Found: C, 39.34; H, 6.35. The presence of lattice H_2O has been confirmed by IR and ^1H NMR spectroscopy. The propensity of dirhenium polyhydrides to incorporate water and other lattice solvent molecules has been noted.[7,8,10]

D. Synthesis of Dirhenium Pentahydrides. (i) $[Re_2H_5(dmpm)_3]BF_4$. A small quantity of a 1.5 M solution of dmpm in toluene (0.047 mL, 0.071 mmol) was added to a vessel that contained a solution of 0.044 g of $Re_2H_8(dmpm)_2$ (0.067 mmol) dissolved in 10 mL of CH_2Cl_2. The red color of this solution immediately changed to brown upon addition of the phosphine. After a period of 30 min, 0.01 mL of $HBF_4\cdot Et_2O$ was syringed into the flask, and 1 min later, an excess of diethyl ether was added to precipitate the product. The yellow solid was collected by filtration, washed with diethyl ether, and dried under vacuum; yield 0.031 g (51%). This complex was identified on the basis of the close similarity of its electrochemical and spectroscopic properties to those of the PF_6^- salt (vide infra, section D(ii)).

(ii) $[Re_2H_5(dmpm)_3]PF_6$. A quantity of $Re_2Cl_4(\mu\text{-dmpm})_3$ (0.272 g, 0.295 mmol) was placed in a three-necked round-bottom flask equipped with a stir bar, N_2 gas inlet, and a side arm containing 0.17 g (4.5 mmol) of $LiAlH_4$ (4.5 mmol). The remaining neck was sealed with a rubber septum, the system was purged with N_2 gas, and 15 mL of THF was added to the flask. Following the addition of the $LiAlH_4$, the mixture turned green. This mixture was stirred at room temperature for 2 h and then hydrolyzed with a 5:15 (mL) mixture of H_2O/THF. Upon gentle heating of the mixture for 2 h, its color changed to bright yellow. Insoluble lithium salts were removed by filtration of the mixture through Celite, and a flask containing the filtrate was sealed with a septum. The filtrate was then evaporated under vacuum to give a yellow residue, which was dissolved in a minimum volume of CH_2Cl_2, and the solution was filtered into cold *n*-pentane to give a yellow precipitate; yield 0.170 g. This solid is a salt of the $[Re_2H_5(dmpm)_3]^+$ cation and contains an unidentified anion which can be exchanged with PF_6^- by use of the following procedure. The aforementioned yellow solid was dissolved in 5 mL of water and mixed with a solution of KPF_6 (0.10 g, 0.54 mmol) in 1 mL of water. The yellow precipitate was filtered off, washed with H_2O and diethyl ether, and dried under vacuum. The product can be recrystallized from dichloromethane/diethyl ether; yield 75%. Anal. Calcd for $C_{15}H_{53}F_6O_3P_7Re_2$ (i.e. $[Re_2H_5(dmpm)_3]PF_6\cdot 3H_2O$): C, 18.29; H, 5.44. Found: C, 18.20; H, 5.61. The presence of H_2O was confirmed by a resonance at δ +1.8 in the ^{1}NMR spectrum of a $CDCl_3$ solution of the complex. This resonance integrates to approximately three H_2O molecules. The propensity of dirhenium polyhydrides to incorporate water and other lattice solvent molecules has been noted.[7,8,10]

The BPh_4^- salt can be isolated by use of a procedure similar to that described above by substituting $NaBPh_4$ for KPF_6. This product was not studied in much detail because of its poor solubility properties.

(iii) $[Re_2D_5(dmpm)_3]PF_6$. A sample of this complex was prepared by a procedure similar to that described in section D(ii) but with use of $LiAlD_4$ in place of $LiAlH_4$ and D_2O in place of H_2O; yield 76%.

(iv) $[Re_2H_5(dppe)_3]BF_4$. A small quantity of $Re_2H_4(dppe)_3$ (0.055 g, 0.035 mmol) was dissolved in 2 mL of CH_2Cl_2 to give a dark red solution, and 0.006 mL of $HBF_4\cdot Et_2O$ was added. After the mixture had been stirred for ca. 3 min, diethyl ether (30 mL) was added to the dark green solution. The gray-green precipitate that formed was filtered off, washed with diethyl ether, and dried in vacuo; yield 0.049 g (84%). Anal. Calcd for $C_{79}H_{79}BCl_2F_4P_6Re_2$ (i.e. $[Re_2H_5(dppe)_3]BF_4\cdot CH_2Cl_2$): C, 54.39; H, 4.57. Found: C, 54.70; H, 4.54.

(v) $[Re_2H_5(dppe)_2(dppm)]BF_4$. A solution of $Re_2H_4(dppe)_2(dppm)$ (0.032 g, 0.030 mmol) in 5 mL of THF was treated with 0.01 mL of $HBF_4\cdot Et_2O$, whereupon the color of the reaction mixture changed from brown to green. It was stirred for 5 min and then treated with an excess of diethyl ether to give a green precipitate. The product was filtered off and washed with 5 mL of diethyl ether; yield 0.021 g (62%). The same product was obtained when NH_4PF_6 was used in place of $HBF_4\cdot Et_2O$ and the reaction time was extended to 24 h. While repeated attempts to obtain a satisfactory microanalysis were unsuccessful, deprotonation of this complex to regenerate the tetrahydride starting material in good yield indicates that this formulation is correct. This deprotonation reaction was carried out by treating the product (0.050 g, 0.030 mmol) with 0.2 mL of the organic base DBU (1,8-diazabicyclo[5.4.0]-7-undecene) in 5 mL of THF. The solution was evaporated to <2 mL and an excess of methanol added to precipitate the product; yield 0.042 g (89%).

(vi) $[Re_2H_5(PMe_3)_4(dppe)]BF_4$. A small quantity of $Re_2H_4(PMe_3)_4(dppe)\cdot 4H_2O$ (0.021 g, 0.018 mmol) was dissolved in 5 mL of THF and this solution treated with 0.01 mL of $HBF_4\cdot Et_2O$. The orange solution turned green upon addition of the acid, and after 5 min an excess of diethyl ether was added to precipitate a green solid. The product was filtered off and washed with 5 mL of diethyl ether; yield 0.016 g (71%). Identification of the complex as $[Re_2H_5(PMe_3)_4(dppe)]BF_4$ was based upon its electrochemical and NMR spectral properties, which were the same as those observed for the sample of $[Re_2H_5(PMe_3)_4(dppe)]PF_6$ (vide infra, section D(vii)).

(vii) $[Re_2H_5(PMe_3)_4(dppe)]PF_6$. Approximately stoichiometric quantities of $Re_2H_8(PMe_3)_4$ (0.050 g, 0.073 mmol), dppe (0.034 g, 0.085 mmol), and KPF_6 (0.020 g, 0.11 mmol) were placed in a round-bottom flask. The flask was sealed, the contents were purged with N_2 gas, and 5 mL of methanol was added by syringe. The reaction mixture was stirred at room temperature for 24 h, after which the solvent was evaporated under a stream of N_2 gas. Extraction of the residue into 1 mL of CH_2Cl_2 and the addition of diethyl ether to this extract yielded a green product,

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(22) Anderson, L. B.; Cotton, F. A.; Falvello, L. R.; Harwood, W. S.; Lewis, D.; Walton, R. A. *Inorg. Chem.* **1986**, *25*, 3637.

(23) Ara, I.; Fanwick, P. E.; Walton, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 1429.

Table I. Crystallographic Data for $[Re_2H_5(dppe)_3]ReO_4$ (**1**), $[ReO_2(dppe)_2]ReO_4$ (**2**), and $[Re_2H_5(dmpm)_3]PF_6$ (**3**)

	1	**2**	**3**
chem formula	$Re_3P_6O_4C_{78}H_{77}$	$Re_2P_4O_6C_{52}H_{48}$	$Re_2P_7F_6C_{15}H_{47}$
fw	1822.92	1265.25	930.75
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	12.177 (1)	9.805 (2)	9.288 (1)
b, Å	23.152 (2)	14.500 (3)	24.515 (3)
c, Å	26.843 (4)	17.572 (4)	13.761 (3)
β, deg	100.32 (1)	92.89 (2)	93.23 (1)
V, $Å^3$	7445 (3)	2495 (2)	3128 (1)
Z	4	2	4
T, °C	21	21	−100
λ, Å (Mo Kα)	0.710 73	0.710 73	0.710 73
ρ_{calcd}, g cm^{-3}	1.626	1.684	1.976
μ(Mo Kα), cm^{-1}	51.05	50.86	82.32
transm coeff	1.00–0.85	1.00–0.75	1.00–0.68
R^a	0.048	0.067	0.030
$R_w{}^b$	0.060	0.086	0.039

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

which was filtered off and washed with diethyl ether; yield 0.046 g (51%). Anal. Calcd for $C_{38.5}H_{66}ClF_6P_7Re_2$ (i.e. $[Re_2H_5(PMe_3)_4(dppe)]PF_6 \cdot {}^1/_2CH_2Cl_2$): C, 36.47; H, 5.26. Found: C, 36.34; H, 5.39. The presence of a small amount of lattice CH_2Cl_2 was confirmed by a resonance at δ +5.4 in the ^1H NMR spectrum of a $CDCl_3$ solution of the complex.

(viii) $[Re_2H_5(PMe_3)_4(dppm)]PF_6$. A procedure similar to that described in section D(vii) was used to prepare this complex from 0.081 g of $Re_2H_8(PMe_3)_4$ (0.12 mmol), 0.052 g of dppm (0.13 mmol), and 0.025 g of KPF_6 (0.15 mmol); yield 0.042 g (30%). Anal. Calcd for $C_{37}H_{63}F_6P_7Re_2$: C, 36.69; H, 5.25. Found: C, 36.96; H, 5.96.

Preparation of Single Crystals for X-ray Structure Analyses. Crystals of the complexes $[Re_2H_5(dppe)_3]ReO_4$ (**1**) and $[ReO_2(dppe)_2]ReO_4$ (**2**) were obtained serendipitously during unsuccessful attempts to grow single crystals of $Re_2H_8(dppe)_2$ from THF/methanol over a period of several weeks. Samples of $Re_2H_8(dppe)_2$ were dissolved in deoxygenated THF, and these solutions were placed in disposable pipets that had been sealed off at one end. These tubes were placed inside a large test tube that contained a quantity of methanol, the test tube was sealed, and vapor diffusion was allowed to take place slowly. It was noted that after a few days some of the original sample had precipitated from solution as a powder. However, after several weeks, yellow-brown crystals had formed at the surface of the powder. The system was then opened (with a brief exposure to the atmosphere) in order to examine the crystals under a microscope and was repurged with N_2 and allowed to remain at room temperature for several more days. By this time a few additional crystals had formed in the tubes at the surface of the solvent. These crystals were dark orange and were apparently of a type different from those of the first batch. Both sets of crystals were found to be suitable for X-ray crystallographic analysis. However, neither batch turned out to be crystals of the original sample, $Re_2H_8(dppe)_2$. The dark orange crystals were found to be those of $[Re_2H_5(dppe)_3]ReO_4$ (**1**), while the yellow-brown crystals proved to be $[ReO_2(dppe)_2]ReO_4$ (**2**). Crystals of a different salt of the $[Re_2H_5(dppe)_3]^+$ cation, $[Re_2H_5(dppe)_3]BF_4$, were grown from dichloromethane/n-heptane. Suitable crystals of $[Re_2H_5(dmpm)_3]PF_6$ (**3**) were obtained by the slow diffusion of isopropyl ether into a solution of this complex in 1,2-dichloroethane.

X-ray Structure Analyses. The structures of $[Re_2H_5(dppe)_3]ReO_4$ (**1**), $[ReO_2(dppe)_2]ReO_4$ (**2**), and $[Re_2H_5(dmpm)_3]PF_6$ (**3**) were determined by the application of standard procedures. Data for **1** and **2** were collected at room temperature and those for **3** at −100 °C. The basic crystallographic parameters are listed in Table I. The cell constants are based on 25 reflections with 21.8° < θ < 22.5°, 18.6° < θ < 20.7°, and 23.0 < θ < 25.0° for **1**–**3**, respectively. Three standard reflections were measured after every 5000 s of beam exposure during data collection, but we observed no systematic variations in decay of these standards. Calculations were performed on a microVAX II computer using the Enraf-Nonius structure determination package. The crystals of **1**–**3** were all found to belong to the monoclinic space group $P2_1/n$ (No. 14). Lorentz and polarization corrections were applied to all three sets of data, and an empirical absorption correction[24] was applied in all cases. The linear absorption coefficient used was 51.05 cm^{-1} for **1**, 50.86 cm^{-1} for **2**, and 82.32 cm^{-1} for **3**. No corrections for extinction were applied.

The structures were solved by the use of the Patterson heavy-atom method which revealed the positions of the Re atoms. The remaining non-hydrogen atoms were located in succeeding difference Fourier syntheses. There was no evidence for the presence of lattice solvent molecules in any of the three structures. The structures were refined by full-matrix least-squares techniques where the function minimized was $\sum w(|F_o| - |F_c|)^2$, where w is the weighting factor defined as $w = 1/\sigma^2(F_o)$.

The hydride ligands were not located in the structure of **1**, their presence being inferred from the spectroscopic properties of this complex, and the hydrogen atoms of the dppe ligands in **1** were not included. During the course of the structure refinement, two areas of electron density were located about general positions which we assumed were associated with lattice solvent molecules and/or an anionic species. The former possibility was eliminated, since we found no evidence for the presence of THF or methanol solvent from the ^1H NMR spectrum of the batch of crystals used, while the presence of an anionic species was supported by the IR spectrum, which showed the ν(Re–O) mode of ReO_4^- at 905 (s) cm^{-1}. For reasons cited below, we assumed that there was one anion per formula unit. In the refinement the rhenium atoms of the perrhenate anions were constrained to have multiplicities such that $M_{Re(3)} = 100 - M_{Re(4)}$. Although convergence was achieved with multiplicities of 76% for Re(3) and 24% for Re(4), these atoms had rather large temperature factors and the oxygen atoms associated with each ReO_4^- could not be identified. It is uncertain whether this is a consequence of the large thermal motions of the rhenium atoms or whether it reflects a disorder of the anions. All atoms were refined anisotropically, and corrections for anomalous scattering were applied.[25] The largest peak in the final difference Fourier map was 1.93 e/$Å^3$ and was near one of these perrhenate rhenium atoms. On the basis of this structure analysis and the spectroscopic properties of this complex, it is accorded the formulation $[Re_2H_5(dppe)_3]ReO_4$. Further support for this formulation was provided by our attempted characterization of an authentic sample of $[Re_2H_5(dppe)_3]BF_4$. The crystal selected was isomorphous with that of **1**: space group $P2_1/n$, a = 12.199 (7) Å, b = 23.545 (7) Å, c = 26.934 (7) Å, β = 100.32 (1)°, V = 7445 (3) $Å^3$, and Z = 4. While refinement of this structure showed the cation to be well-behaved and to be *identical in all respects* with that present in **1**, our attempts to refine the anion were unsuccessful, probably as a result of a disorder problem, and we abandoned the refinement at a stage where R = 0.062 (R_w = 0.081). However, this result is good evidence for our structural conclusions concerning the correct identity of **1**.

The structure refinement of **2** was routine, with the mononuclear *trans*-$[ReO_2(dppe)_2]^+$ cation residing at an inversion center and the perrhenate anion at a general position. Hydrogen atoms of the dppe ligands were not included. Refinement of ReO_4^- was not very satisfactory and gave rather disparate Re–O distances. This may reflect a disorder problem. However, since this is a known compound and is not of special significance in the present study, further refinement was not pursued. All atoms, except the oxygen atoms of the perrhenate anion, were refined anisotropically, and corrections for anomalous scattering were applied to these atoms.[25] The largest peak in the final difference Fourier map was 3.20 e/$Å^3$ and was a ghost of the perrhenate rhenium atom.

In the refinement of **3**, the five hydride ligands were located following anisotropic refinement of all non-hydrogen atoms. Hydrogen atoms of the dmpm ligands were included at fixed positions, which were calculated by assuming idealized geometry and a C–H bond distance of 0.95 Å. We assumed that the value of B(H), i.e., the isotropic equivalent thermal parameter for the hydrogen atoms, was equal to $1.3[B_{eqv}(C)]$ at the time of the inclusion of this parameter in the refinement procedure. While these hydrogen atoms were used in the calculation of F_c, their positions were not refined. All non-hydrogen atoms were refined anisotropically, and corrections for anomalous scattering were applied to these atoms.[25] The largest peak in the final difference Fourier map (1.67 e/$Å^3$) was at nonbonding distances to the cation and anion.

Positional parameters and their errors for the important atoms of **1**–**3** are listed in Tables II–IV. Some important intramolecular bond distances and angles for these structures are given in Tables V–VII. Tables giving full details of the crystal data and data collection parameters (Tables S1–S3), the positional parameters for all atoms (Tables S4–S7), the

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

(25) (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 II. Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) for the Non-Phenyl Atoms of **1** and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*
Re(1)	0.45079 (4)	0.03340 (2)	0.73622 (2)	2.19 (1)
Re(2)	0.43063 (4)	−0.02907 (3)	0.81346 (2)	2.25 (1)
Re(3)	0.3341 (2)	0.25886 (9)	0.51655 (7)	10.17 (5)
Re(4)	0.5592 (6)	0.2310 (2)	0.4447 (3)	11.3 (2)
P(11)	0.4567 (3)	−0.0275 (2)	0.6673 (1)	2.52 (7)
P(12)	0.2859 (3)	0.0831 (2)	0.6968 (1)	2.74 (8)
P(13)	0.5281 (3)	0.1223 (2)	0.7153 (1)	2.81 (8)
P(21)	0.3993 (3)	−0.1238 (2)	0.7817 (1)	2.48 (8)
P(22)	0.5774 (3)	−0.0555 (2)	0.8778 (1)	3.04 (8)
P(23)	0.3504 (3)	−0.0070 (2)	0.8850 (1)	3.19 (8)
C(113)	0.396 (1)	−0.0986 (6)	0.6770 (5)	2.9 (3)
C(123)	0.320 (1)	0.1463 (7)	0.6602 (7)	4.2 (4)
C(133)	0.419 (1)	0.1776 (7)	0.6922 (6)	3.5 (4)
C(213)	0.459 (1)	−0.1342 (6)	0.7234 (5)	2.6 (3)
C(223)	0.528 (1)	−0.074 (1)	0.9375 (6)	6.0 (5)
C(233)	0.415 (2)	−0.0522 (9)	0.9389 (7)	5.9 (5)

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

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

atom	*x*	*y*	*z*	*B*
Re	0	0	0	3.13 (1)
P(1)	0.0711 (4)	−0.1425 (3)	0.0713 (2)	3.59 (7)
P(2)	−0.1346 (4)	−0.1179 (3)	−0.0739 (2)	3.62 (7)
O(1)	0.1395 (9)	−0.0009 (7)	−0.0611 (5)	4.4 (2)
C(1)	−0.053 (2)	−0.236 (1)	0.045 (1)	4.9 (3)
C(2)	−0.182 (2)	−0.200 (1)	−0.0015 (8)	4.5 (3)
Re(2)	0.3497 (2)	−0.0091 (1)	0.5497 (1)	7.37 (4)
O(21)	0.290 (5)	0.091 (4)	0.559 (3)	16 (2)*
O(22)	0.273 (4)	−0.061 (3)	0.491 (2)	10.2 (9)*
O(23)	0.286 (6)	−0.070 (4)	0.611 (3)	16 (2)*
O(24)	0.537 (7)	−0.016 (4)	0.571 (4)	18 (2)*

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

anisotropic thermal parameters (Tables S8–S10), and complete bond distances (Tables S11–S13) and bond angles (Tables S14–S16) for **1**–**3**, as well as figures showing the full atomic numbering schemes for the cations of **1** and **2** (Figures S1 and S2), are available as supplementary material.

Physical Measurements. IBM Instruments IR/32 and Perkin-Elmer 1800 FTIR spectrometers were used to record the IR spectra of compounds as Nujol mulls supported on KBr plates in the region 4800–400 cm^{-1}. Electrochemical measurements were carried out by the use of a Bioanalytical Systems Inc. Model CV-1A instrument on dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. A Pt-bead working electrode and a Pt-wire auxiliary electrode were utilized. $E_{1/2}$ 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, the ferrocenium/ferrocene couple is at $E_{1/2} = +0.47$ V vs Ag/AgCl. Bulk electrolyses were carried out with the use of a Pt-gauze working electrode and a Bioanalytical Systems Inc. Model SP-2 potentiostat. ^{1}H and ^{31}P NMR spectra were recorded on a Varian XL-200 spectrometer. Proton resonances were referenced internally to the residual protons in the incompletely deuteriated solvent (δ +7.20 in C_6D_6, δ +7.10 (C_6H_5) and δ +2.10 (CH_3) in C_7D_8, δ +5.35 in CH_2Cl_2, δ +4.8 in D_2O, and δ +2.17 in $(CD_3)_2CO$ solvent). Phosphorus resonances were referenced externally to 85% H_3PO_4. X-Band ESR spectra were recorded at ca. −160 °C with the use of a Varian E-109 spectrometer. Conductivity measurements were made on solutions of the samples at a concentration of ca. 1.0×10^{-3} M utilizing an Industrial Instruments Inc. Model RC-16B2 conductivity bridge.

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

Table IV. Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) for All Atoms except the Hydrogen Atoms of the dmpm Ligands of **3** and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*
Re(1)	0.52978 (3)	0.11106 (1)	0.32164 (2)	1.740 (5)
Re(2)	0.17776 (3)	0.05922 (1)	0.28739 (2)	1.805 (5)
P(11)	0.4858 (2)	0.15217 (8)	0.1638 (1)	2.27 (4)
P(12)	0.6023 (2)	0.02155 (8)	0.2828 (1)	2.17 (4)
P(13)	0.4300 (2)	0.17441 (8)	0.4293 (1)	2.16 (4)
P(21)	0.1740 (2)	0.10562 (8)	0.1334 (1)	2.39 (4)
P(22)	0.2902 (2)	−0.02337 (8)	0.2457 (1)	2.16 (4)
P(23)	0.1186 (2)	0.12666 (9)	0.4029 (1)	2.39 (4)
C(1B)	0.3495 (8)	0.1176 (4)	0.0835 (6)	2.8 (2)
C(2B)	0.4710 (8)	−0.0326 (3)	0.3017 (6)	2.4 (1)
C(3B)	0.2677 (8)	0.1502 (3)	0.4838 (5)	2.6 (2)
C(111)	0.6391 (9)	0.1534 (4)	0.0861 (6)	3.8 (2)
C(112)	0.433 (1)	0.2241 (3)	0.1517 (6)	3.6 (2)
C(121)	0.6685 (9)	0.0067 (3)	0.1630 (6)	3.6 (2)
C(122)	0.7504 (8)	−0.0050 (3)	0.3601 (6)	3.0 (2)
C(131)	0.548 (1)	0.1857 (4)	0.5386 (6)	3.5 (2)
C(132)	0.385 (1)	0.2445 (3)	0.3963 (7)	3.5 (2)
C(211)	0.0811 (9)	0.0702 (4)	0.0304 (7)	4.1 (2)
C(212)	0.083 (1)	0.1714 (4)	0.1167 (7)	4.3 (2)
C(221)	0.313 (1)	−0.0438 (4)	0.1198 (7)	3.8 (2)
C(222)	0.2036 (9)	−0.0839 (4)	0.2901 (8)	3.9 (2)
C(231)	0.025 (1)	0.1894 (4)	0.3668 (8)	4.2 (2)
C(232)	−0.0025 (9)	0.1019 (4)	0.4923 (6)	3.5 (2)
H(B)	0.373 (8)	0.100 (3)	0.289 (6)	1 (2)*
H(11)	0.501 (9)	0.080 (4)	0.424 (6)	1 (2)*
H(12)	0.66 (1)	0.108 (4)	0.411 (8)	4 (3)*
H(21)	0.25 (1)	0.030 (5)	0.402 (8)	3 (3)*
H(22)	0.09 (1)	0.013 (4)	0.344 (6)	2 (2)*
P(1000)	0.2968 (2)	0.17943 (7)	0.7956 (1)	2.08 (4)
F(1001)	0.3196 (9)	0.1410 (3)	0.7053 (4)	6.6 (2)
F(1002)	0.2989 (9)	0.2317 (2)	0.7346 (5)	7.4 (2)
F(1003)	0.1323 (9)	0.1737 (4)	0.772 (1)	13.9 (4)
F(1004)	0.289 (1)	0.1244 (3)	0.8556 (5)	12.0 (3)
F(1005)	0.4582 (9)	0.1817 (4)	0.8177 (9)	12.3 (3)
F(1006)	0.274 (1)	0.2138 (3)	0.8890 (5)	9.4 (2)

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

Table V. Important Bond Distances (Å) and Bond Angles (deg) for the Cation of **1**[a]

	Bond Distances		
Re(1)–Re(2)	2.5755 (6)	Re(2)–P(21)	2.360 (3)
Re(1)–P(11)	2.336 (3)	Re(2)–P(22)	2.334 (3)
Re(1)–P(12)	2.391 (3)	Re(2)–P(23)	2.361 (3)
Re(1)–P(13)	2.373 (3)		
	Bond Angles		
Re(1)–Re(2)–P(21)	105.27 (8)	Re(2)–Re(1)–P(11)	108.61 (8)
Re(1)–Re(2)–P(22)	124.92 (9)	Re(2)–Re(1)–P(12)	115.66 (8)
Re(1)–Re(2)–P(23)	130.24 (9)	Re(2)–Re(1)–P(13)	140.97 (8)
P(21)–Re(2)–P(22)	94.4 (1)	P(11)–Re(1)–P(12)	94.7 (1)
P(21)–Re(2)–P(23)	115.6 (1)	P(11)–Re(1)–P(13)	105.5 (1)
P(22)–Re(2)–P(23)	80.1 (1)	P(12)–Re(1)–P(13)	79.3 (1)

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

Results

The present study was carried out with the main objectives of (i) examining the reactivity of $Re_2H_8(dppe)_2$ toward dppe and other phosphines and (ii) designing routes to dirhenium polyhydride complexes that contained the dmpm ligand. Accordingly, these results are presented separately.

(a) Reactions of $Re_2H_8(dppe)_2$ with Phosphines. The title complex reacts with an excess of dppe in both methanol and benzene to afford the red-brown tetrahydrido complex $Re_2H_4(dppe)_3$ in ca. 70% yield. This complex forms nonconducting solutions in acetone. The treatment of this complex with

Table VI. Important Bond Distances (Å) and Bond Angles (deg) for **2**[a]

Bond Distances			
Re(1)–P(1)	2.497 (3)	Re(2)–O(1)	1.781 (6)
Re(1)–P(2)	2.485 (3)		
Bond Angles			
P(1)–Re(1)–P(1)	180.0	P(2)–Re(1)–P(2)	180.0
P(1)–Re(1)–P(2)	79.7 (1)	P(2)–Re(1)–O(1)	94.8 (2)
P(1)–Re(1)–P(2)	100.3 (1)	P(2)–Re(1)–O(1)	85.2 (2)
P(1)–Re(1)–O(1)	95.3 (3)	O(1)–Re(1)–O(1)	180.0
P(1)–Re(1)–O(1)	84.7 (3)		

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

Table VII. Important Bond Distances (Å) and Bond Angles (deg) for the Cation of **3**[a]

Bond Distances			
Re(1)–P(11)	2.408 (2)	Re(2)–P(21)	2.404 (2)
Re(1)–P(12)	2.365 (2)	Re(2)–P(22)	2.363 (2)
Re(1)–P(13)	2.371 (2)	Re(2)–P(23)	2.379 (2)
Re(1)–H(B)	1.53 (7)	Re(2)–H(B)	2.06 (7)
Re(1)–H(11)	1.64 (8)	Re(2)–H(21)	1.8 (1)
Re(1)–H(12)	1.7 (1)	Re(2)–H(22)	1.62 (8)
Bond Angles[b]			
Re(2)–Re(1)–P(11)	85.48 (4)	P(12)–Re(1)–H(B)	92 (3)
Re(2)–Re(1)–P(12)	84.77 (4)	P(12)–Re(1)–H(11)	80 (3)
Re(2)–Re(1)–P(13)	85.83 (4)	P(12)–Re(1)–H(12)	86 (3)
Re(2)–Re(1)–H(11)	76 (3)	P(13)–Re(1)–H(B)	85 (3)
Re(2)–Re(1)–H(12)	135 (3)	P(13)–Re(1)–H(11)	71 (3)
P(11)–Re(1)–P(12)	102.73 (7)	P(13)–Re(1)–H(12)	82 (3)
P(11)–Re(1)–P(13)	103.72 (7)	H(B)–Re(1)–H(11)	88 (4)
P(11)–Re(1)–H(B)	73 (3)	H(B)–Re(1)–H(12)	148 (4)
P(11)–Re(1)–H(11)	161 (3)	H(11)–Re(1)–H(12)	60 (4)
P(11)–Re(1)–H(12)	139 (3)	Re(1)–H(B)–Re(2)	156 (5)
P(12)–Re(1)–P(13)	151.07 (6)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Angles about Re(1) only are given. The corresponding angles about Re(2) are essentially the same and are provided in the supplementary material.

$HBF_4{\cdot}Et_2O$ yields the gray-green salt $[Re_2H_5(dppe)_3]BF_4$, which contains the very stable $[Re_2H_5(dppe)_3]^+$ cation. We have been unable to deprotonate this pentahydride cation (NEt_3, KH, $LiEt_3BH$, *n*-BuLi, and KO-*t*-Bu were used) to re-form the parent tetrahydride. The mixed-phosphine complexes $Re_2H_4(dppe)_2(dppm)$ and $[Re_2H_5(dppe)_2(dppm)]BF_4$ have been prepared by use of procedures analogous to those described above (see eqs 1 and 2). However, in the case of $[Re_2H_5(dppe)_2(dppm)]^+$ deprotonation to regenerate $Re_2H_4(dppe)_2(dppm)$ can be accomplished through the use of the organic base DBU. Solutions of the pentahydride complexes in acetone have conductivities in accord with 1:1 electrolyte behavior ($\Lambda_m \approx 125\ \Omega^{-1}\ cm^2\ mol^{-1}$).

$$\mathrm{Re_2H_8(dppe)_2 + LL \rightarrow Re_2H_4(dppe)_2(LL) + 2H_2} \quad (1)$$

$$\mathrm{Re_2H_4(dppe)_2(LL) + HBF_4 \rightarrow [Re_2H_5(dppe)_2(LL)]BF_4} \quad (2)$$

$$\mathrm{LL = dppe,\ dppm}$$

We were unable to obtain a pure product of composition $Re_2H_4(dppe)_2(PMe_3)_2$ upon reacting $Re_2H_8(dppe)_2$ with PMe_3 in THF. Although the product displayed a deceptively simple ^1H NMR spectrum (in C_6D_6), with only a *single* broad hydride resonance at δ −7.4, $^{31}P\{^1H\}$ NMR spectroscopy indicated that it was a mixture. A better defined mixed dppe–PMe_3 complex was obtained by the alternative procedure of reacting $Re_2H_8(PMe_3)_4$ with dppe.[26] This produced the red-orange compound $Re_2H_4(PMe_3)_4(dppe)$ in fairly low yield (24%), which could be converted to green $[Re_2H_5(PMe_3)_4(dppe)]BF_4$ upon treatment with $HBF_4{\cdot}Et_2O$. The PF_6^- salt of this same cation was prepared by stirring a mixture of $Re_2H_8(PMe_3)_4$, dppe, and KPF_6 in methanol, a strategy that works equally well in preparing $[Re_2H_5(PMe_3)_4(dppm)]PF_6$ (eq 3).[27] Surprisingly, we were not successful in obtaining the pure tetrahydride $Re_2H_4(PMe_3)_4(dppm)$ from the reaction of $Re_2H_8(PMe_3)_4$ with dppm.

$$\mathrm{Re_2H_8(PMe_3)_4 + LL + PF_6^- \xrightarrow{MeOH} [Re_2H_5(PMe_3)_4(LL)]PF_6 + 2H_2} \quad (3)$$

$$\mathrm{LL = dppe,\ dppm}$$

The more important electrochemical data and *room-temperature* spectroscopic properties of these dppe- and dppm-containing polyhydride complexes are summarized in Table VIII. In some instances, temperature-range NMR spectra data were also recorded.

The ^1H NMR spectra of $Re_2H_4(dppe)_3$ and $Re_2H_4(dppe)_2(dppm)$ in CD_2Cl_2 at room temperature each show two broad Re–*H* resonances (Table VIII), the downfield resonance being assigned to bridging hydrido ligands and the upfield resonance to terminal hydride ligands.[28] The ratio of bridging to terminal Re–H ligands in $Re_2H_4(dppe)_3$ is 2:2 and therefore differs from the ratio for $Re_2H_4(dppe)_2(dppm)$, which is 3:1. While the spectrum of $Re_2H_4(dppe)_2(dppm)$ is unaffected by cooling the solution to −80 °C, that of $Re_2H_4(dppe)_3$ is temperature dependent. This spectrum was examined over a temperature range of +70 to −70 °C (in C_6D_6 from +70 to +20 °C and in CD_2Cl_2 from +30 to −70 °C). At the low-temperature limit of −70 °C, the hydride resonances appear as two broad singlets of similar intensity at δ −4.3 and −11.4. As the temperature is raised, these resonances broaden slowly (and shift slightly) until coalescence is reached (by ca. +70 °C). The room-temperature $^{31}P\{^1H\}$ NMR spectrum of $Re_2H_4(dppe)_3$ (in CD_2Cl_2) exhibits broad resonances at δ +49.2 and +46.9, the former being the much broader of the two. As the temperature is lowered to −70 °C, these resonances shift downfield slightly. The peak at δ +46.9 shifts to δ +49.4 but otherwise remains essentially unchanged, while the other resonance splits into two sharper resonances at δ +52.9 and +52.4. The three resonances seen at −70 °C are of similar intensity, thereby suggesting the presence of three pairs of inequivalent phosphorus atoms. The chemical shifts of these phosphorus resonances are characteristic of chelating dppe ligands in dirhenium complexes.[29] Note that the downfield shift of these resonances with a decrease in temperature may reflect the presence of a small amount of paramagnetic impurity, probably $[Re_2H_4(dppe)_3]^+$. The cyclic voltammetric properties of $Re_2H_4(dppe)_3$ show the presence of a very accessible one-electron oxidation ($E_{1/2}(ox) = -0.54$ V vs Ag/AgCl in 0.1 M TBAH/CH_2Cl_2), behavior which is closely related to that exhibited by the other tetrahydrido complexes $Re_2H_4(dppe)_2(dppm)$ and Re_2H_4-

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[26] The formation of $Re_2H_4(PMe_3)_4(dppe)$ was monitored by ^1H NMR spectroscopy of a solution containing 1:1 stoichiometric amounts of $Re_2H_8(PMe_3)_4$ and dppe in deoxygenated C_6D_6. The spectrum was recorded after reaction times of 0.5, 1, and 48 h. The formation of the tetrahydride was clearly shown by the growth of a hydride resonance at δ −7.9, but significant contamination by $Re_2H_6(PMe_3)_5$ (δ −8.7, hextet, $^2J_{PH} = 12$ Hz)[15] was also indicated. The latter species is formed[15] by the reaction of $Re_2H_8(PMe_3)_4$ with small amounts of free PMe_3 which are released in the system.

[27] The protonation of neutral dirhenium polyhydrides by methanol is well documented.[15]

[28] This chemical shift between Re–H–Re and Re–H units is well established[2a,11,14–16,20] and is quite reliable for determining the relative numbers of bridging and terminal hydride ligands.

[29] Cutler, A. R.; Derringer, D. R.; Fanwick, P. E.; Walton, R. A. *J. Am. Chem. Soc.* **1988**, *110*, 5024.

Table VIII. Electrochemical and Spectroscopic Properties of Dirhenium Tetrahydride and Pentahydride Complexes with Bidentate Phosphines

complex	CV half-wave pot., V[a,b] $E_{p,a}$	$E_{1/2}$(ox)[b]	$E_{1/2}$(ox)[b]	IR, cm^{-1}:[c] ν(Re–H)	^{1}H NMR, δ:[d] Re–H	^{31}P{^{1}H} NMR, δ[d,e]	solvent[f]
$Re_2H_4(dppe)_3$	+0.23		−0.54 (150)	1974 w, br, 1892 w, br, 1810 w, br	−4.7 s (1), −13.1 s (1)	+49.4 s (2), +46.9 s (1)	CD_2Cl_2
$[Re_2H_5(dppe)_3]BF_4$		+1.00 (90)	+0.32 (90)	1968 vw, br, 1830 vw, br, 1772 vw	−7.35 s	+59.4 s (2), +22.7 s (1)	CD_2Cl_2
$Re_2H_4(dppe)_2(dppm)$	+0.04[g]		−0.56 (120)	1892 w, 1810 vw, 1774 vw	−6.0 s (3), −7.7 s (1)	+55.9 s (2), +0.6 s (1)	CD_2Cl_2
$[Re_2H_5(dppe)_2(dppm)]BF_4$	+1.30	+1.14[h]	+0.28 (110)	1966 vw, 1898 vw, 1814 vw	−6.0 s	+57.9 s (2), +1.1 s (1)	CD_2Cl_2
$Re_2H_4(PMe_3)_4(dppe)$	−0.02		−0.81 (110)	1920 w, br	−7.9 s	+69.6 s (2), −29.3 s (1), −33.15 s (3)	C_6D_6
$[Re_2H_5(PMe_3)_4(dppe)]PF_6$		+0.85[h]	+0.06 (120)	2026 w, 1970 br, sh, 1902 vw, 1832 vw	−6.8 s	+64.5 d (2),[j] −31.5 s (3), −37.7 t (1)[j]	CD_2Cl_2
$[Re_2H_5(PMe_3)_4(dppm)]PF_6$	+1.42	+0.75[h]	+0.04 (110)	1990 w, br, 1888 w	−6.3 s	+10.5 s (1), −21.8 s (2)	CD_2Cl_2
$[Re_2H_5(dmpm)_3]PF_6$		+0.94[h]	+0.62[h]	2008 m, 1940 m–s, 1916 m–s, 1856 m, br	−8.4 sp[i]	−28.7 s	CD_2Cl_2

[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 a sweep rate of 200 mV s^{-1}. [b] Numbers in parentheses are ΔE_p (i.e. $E_{p,a} - E_{p,c}$) in mV. [c] Recorded as Nujol mulls. For complexes that contain the BF_4^- anion a ν(B–F) mode is present at ca. 1060 cm^{-1}, while for those with the PF_6^- anion there is a ν(P–F) mode at ca. 840 cm^{-1}. [d] Spectra recorded at room temperature. For temperature-range data see text. Abbreviations are as follows: s = singlet, d = doublet, t = triplet, sp = septet. Numbers in parentheses signify the relative intensities of the signals in each spectrum. [e] For compounds that contain the PF_6^- anion an additional resonance (a septet) is present at δ −144.0 (±0.2). [f] Solvent used in the NMR spectral measurements. [g] Other irreversible oxidation processes at +0.21 and +1.00 V. [h] $E_{p,a}$ value given. [i] $^2J_{PH}$ = 9.2 Hz. [j] J_{PP} = 12 Hz.

$(PMe_3)_4(dppe)$ (Table VIII). The exposure of dichloromethane solutions of $Re_2H_4(dppe)_3$ to the air results in a quite rapid color change from orange to blue-green to yellow and complete decomposition of the complex (as monitored by cyclic voltammetry).[30] The blue-green species is probably $[Re_2H_4(dppe)_3]^+$, since the bulk electrolysis of solutions of $Re_2H_4(dppe)_3$ at −0.4 V (i.e. anodic of the process at −0.54 V) generates solutions of the ESR-active paramagnetic cation. An X-band spectrum (recorded at −160 °C) shows a very broad signal centered at g = 2.14 which displays no resolvable hyperfine structure. The diamagnetic neutral tetrahydride is regenerated upon re-reducing this solution at −0.80 V, with retention of structural integrity (as monitored by CV) and loss of this ESR signal. These changes are reproducible through several cycles of oxidation and reduction.

The singlets at δ +59.4 and +22.7 in the room-temperature (+20 °C) ^{31}P{^{1}H} NMR spectrum of $[Re_2H_5(dppe)_3]BF_4$ (Table VIII) are characteristic of chelating and bridging dppe ligands,[31] respectively, while the resonances at δ +57.9 and +1.1 in the spectrum of $[Re_2H_5(dppe)_2(dppm)]BF_4$ (Table VIII) can be assigned to chelating dppe[31] and bridging dppm[29] ligands, respectively. The latter spectrum is therefore similar to that of the parent tetrahydride $Re_2H_4(dppe)_2(dppm)$ (Table VIII). When a CD_2Cl_2 solution of $[Re_2H_5(dppe)_3]BF_4$ was cooled to −40 °C, the phosphorus signal at δ +22.7 remained unchanged while that at δ +59.4 split into singlets of equal intensity at δ +62.6 and +58.6, signifying the presence of inequivalent pairs of phosphorus atoms associated with the dppe ligands. At this same temperature of −40 °C (and below), the ^{1}H NMR spectrum (in CD_2Cl_2) shows a bridging hydride resonance as a broad singlet at δ −6.6 (intensity 3) and an apparent quartet at δ −7.7 (intensity 2), the latter feature being assigned to the terminal hydride ligands that are each coupled to three phosphorus atoms ($^2J_{PH} \approx$ 37 Hz). When this solution is allowed to warm to +30 °C, these hydride resonances coalesce and transform into a broad singlet at δ −7.3 (Figure 1). The ^{1}H NMR spectrum of a solution of this complex in CD_3NO_2 shows that between +30 and +70 °C this singlet remains essentially unchanged. The spectrum of a solution in $(CD_3)_2SO$ also shows a singlet (δ −8.0) at +70 °C.

The structure of the $[Re_2H_5(dppe)_3]^+$ cation was determined from a single-crystal X-ray structure analysis of a crystal of composition $[Re_2H_5(dppe)_3]ReO_4$ that was obtained serendipitously, along with $[ReO_2(dppe)_2]ReO_4$, during attempts to grow single crystals of $Re_2H_8(dppe)_2$ over a period of several weeks.

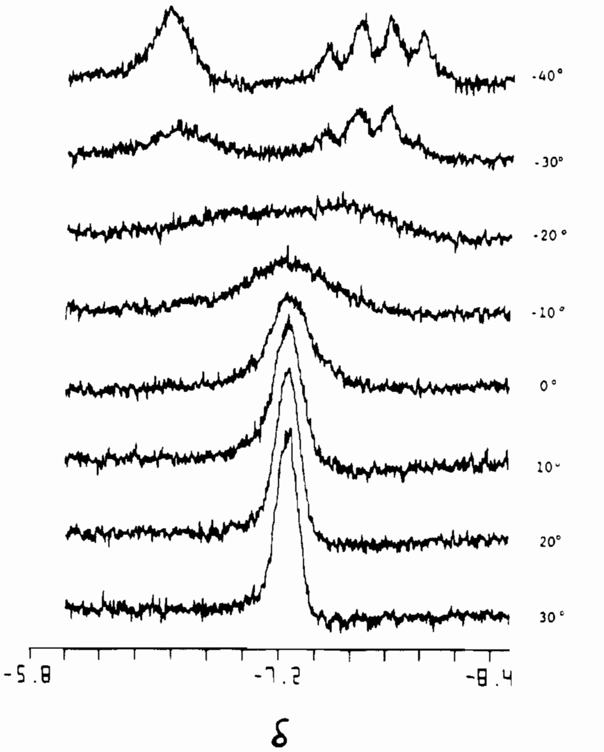

Figure 1. Variable-temperature ^{1}H NMR spectrum of the complex $[Re_2H_5(dppe)_3]BF_4$ (recorded in CD_2Cl_2) in the hydride region. The temperatures vary from +30 °C (bottom) to −40 °C (top). The spectrum does not change significantly at temperatures below −40 °C.

The structures of the $[Re_2H_5(dppe)_3]^+$ (hydride ligands omitted) and *trans*-$[ReO_2(dppe)_2]^+$ cations are shown in Figures 2 and 3, while key structural parameters are provided in Tables V and VI. A crystal structure determination on a crystal of $[Re_2H_5(dppe)_3]BF_4$, from a sample prepared by the protonation of $Re_2H_4(dppe)_3$, showed it to be isostructural with $[Re_2H_5(dppe)_3]ReO_4$, but the structure refinement was terminated because of a serious disorder problem involving the BF_4^- anion. The salt $[ReO_2(dppe)_2]ReO_4$ proved to be a known complex, which, along with other complexes of the type $[ReO_2(dppe)_2]X$, had been reported by Freni et al.[32] in 1967. However, it has not previously been structurally characterized. The IR spectrum of our crystals (Nujol mull, ν(Re=O) at 908 (s) cm^{-1} and ν(O=Re=O) at 786 (s) cm^{-1}) is in excellent agreement with the literature data.[32]

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(30) While the 1-electron oxidant $[Ph_3C]PF_6$ also generates the blue-green species, workup of the resulting solutions gave mainly decomposition products; therefore, this procedure did not provide a convenient route to solid $[Re_2H_4(dppe)_3]PF_6$.

(31) Anderson, L. B.; Bakir, M.; Walton, R. A. *Polyhedron* **1987**, *6*, 1483.

(32) Freni, M.; Giusto, D.; Romiti, P. *Gazz. Chim. Ital.* **1967**, *97*, 833.

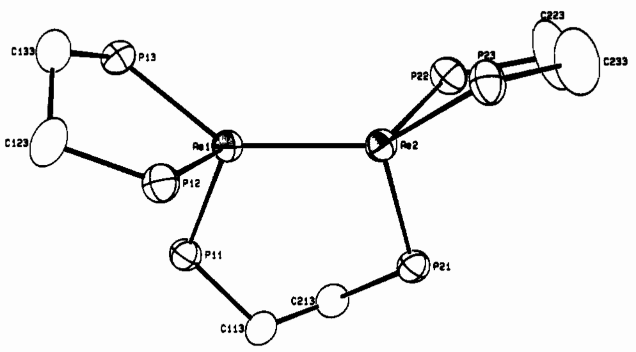

Figure 2. ORTEP view of the rhenium-containing cation of **1** with the phenyl rings omitted. The thermal ellipsoids are drawn at the 50% probability level. The positions of the bridging and terminal hydride ligands were not determined.

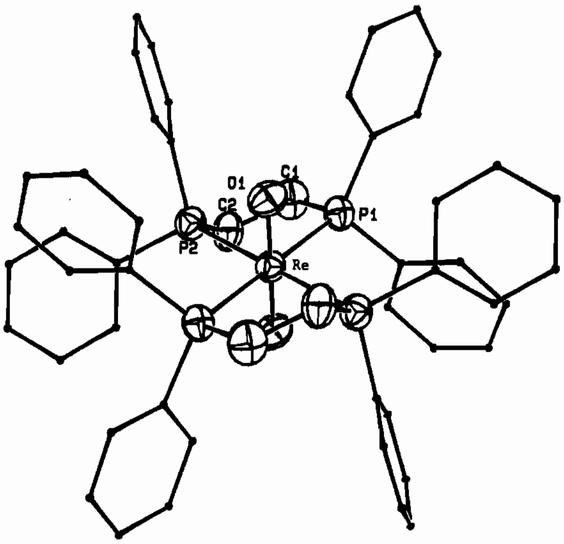

Figure 3. ORTEP view of the rhenium-containing cation of **2**. The thermal ellipsoids are drawn at the 50% probability level except for the carbon atoms of the phenyl rings, which are circles of arbitrary radii.

The mixed PMe_3–dppe and PMe_3–dppm species $Re_2H_4(PMe_3)_4(dppe)$ and $[Re_2H_5(PMe_3)_4(LL)]^+$ (LL = dppe, dppm) were studied in much less detail than the analogous compounds $Re_2H_4(dppe)_2(LL)$ and the salts of the $[Re_2H_5(dppe)_2(LL)]^+$ cations (LL = dppe, dppm). In particular, temperature-range NMR spectral studies were not carried out. The $^{31}P\{^1H\}$ NMR spectrum of a freshly prepared solution of $Re_2H_4(PMe_3)_4(dppe)$ in C_6D_6 displays resonances in a 2:1:3 intensity ratio at δ +69.6, −29.3, and −33.1, which correspond to the phosphorus atoms of a chelating dppe[31] ligand and two inequivalent sets of PMe_3 ligands. For salts of the $[Re_2H_5(PMe_3)_4(dppe)]^+$ cation, a similar assignment can be made for the phosphorus resonances at δ +64.5, −31.5, and −37.7 (intensity ratio 2:3:1) although the chemical shifts of the resonances associated with the inequivalent sets of PMe_3 ligands are now reversed. For $[Re_2H_5(PMe_3)_4(dppm)]PF_6$, a resonance at δ +10.5 in the $^{31}P\{^1H\}$ NMR spectrum is assigned to a bridging dppm ligand,[29] while that at δ −21.8 is attributed to four equivalent PMe_3 ligands. The ^1H NMR spectra of these three PMe_3-containing complexes each consist of a single broad resonance displaying no resolvable P–H coupling (Table VIII).

(b) Reactions of $Re_2H_8(\mu\text{-dmpm})_2$ with dmpm. We examined initially the reactions between $Re_2H_8(\mu\text{-dppm})_2$[7] and dppm with hot benzene as the reaction solvent but found that a mixture resulted which contained at least three hydride species. The components of this mixture were not easily separated, and none appeared to be $Re_2H_4(dppm)_3$, on the basis of an analysis of the NMR spectra. Accordingly, we turned our attention to the reactions of $Re_2H_8(dmpm)_2$ with dmpm, but first needed to design a method for preparing the octahydride starting material. We have previously[6,7] developed a general synthetic route to complexes of the type $Re_2H_8(PR_3)_4$ (PR_3 represents a monodentate or one-half bidentate phosphine) that involves the reaction of the corresponding tetrachloride complexes $Re_2Cl_4(PR_3)_4$ with $LiAlH_4$ in glyme (or THF) at room temperature. However, the compounds $Re_2X_4(\mu\text{-dmpm})_2$ (X = Cl or Br) cannot be prepared by the usual synthetic methods,[29,33] since the much more stable tris-dmpm complexes $Re_2X_4(\mu\text{-dmpm})_3$ are always obtained. However, we have recently prepared[23] the bis-dmpm complex $Re_2(\mu\text{-}O_2CCH_3)Cl_4(\mu\text{-dmpm})_2$, and this compound proved to be a suitable starting material for the synthesis of the dirhenium octahydride $Re_2H_8(dmpm)_2$. Its reaction with $LiAlH_4$ and subsequent hydrolysis of the reaction mixture with THF/H_2O affords the red-brown octahydride (34% yield).

The physical properties of $Re_2H_8(dmpm)_2$ are similar to those of the other known dirhenium octahydrides. Cyclic voltammetric measurements on a 0.1 M $TBAH/CH_2Cl_2$ solution of this polyhydride shows that it displays a reversible process, which corresponds to an oxidation at $E_{1/2}(ox)$ = −0.30 V, and an irreversible oxidation at $E_{p,a}$ = +0.35 V vs Ag/AgCl. These data compare with the values measured for other octahydride complexes of the type $Re_2H_8(PR_3)_4$, which range from $E_{1/2}(ox)$ = −0.63 V and $E_{p,a}$ = +0.34 V when $PR_3 = PEt_3$ to $E_{1/2}(ox)$ = −0.02 V and $E_{p,a}$ = +0.81 V for PR_3 = $^1/_2$ dppe.[7] As expected, the reversible oxidation of $Re_2H_8(dmpm)_2$ occurs at a potential more negative than that of $Re_2H_8(dppm)_2$ ($E_{1/2}$ = −0.11 V) as a consequence of the increased Lewis basicity of the dmpm ligand. The Nujol mull IR spectrum of this polyhydride complex displays two strong ν(Re–H) modes at 1984 and 1954 cm^{-1}, with a shoulder at 2018 cm^{-1}.

A solution of $Re_2H_8(dmpm)_2$ in C_6D_6 gives a simple ^1H NMR spectrum: a singlet at δ +1.64 and a pair of overlapping multiplets at δ +1.72 and +1.77 which correspond to the methyl and methylene protons of the dmpm ligand, respectively. The remaining hydride resonance at δ −6.61 is a binomial pentet ($^2J_{PH}$ = 11.2 Hz) due to coupling to four equivalent phosphorus atoms. This solution gives a singlet in the $^{31}P\{^1H\}$ NMR spectrum at δ +6.2. The phosphorus resonance of $Re_2H_8(dmpm)_2$ is resolved into a nine-line pattern in the selective 2DJ NMR spectrum, and this confirms the presence of eight hydride ligands. The NMR spectral properties of $Re_2H_8(dmpm)_2$ accord with fluxional behavior in solution, as has been found to be the case for $Re_2H_8(dppm)_2$, although in the solid state the latter complex has the structure $Re_2(\mu\text{-}H)_2H_6(\mu\text{-dppm})_2$.

It is not surprising that $Re_2H_8(dmpm)_2$, like its dppe analogue, reacts with excess phosphine ligand. However, the major product is the extraordinarily stable $[Re_2H_5(dmpm)_3]^+$ cation rather than $Re_2H_4(dmpm)_3$; we have been unable to isolate the tetrahydride because of the facility with which it is protonated. The preparation of $[Re_2H_5(dmpm)_3]^+$ is most conveniently accomplished by the reaction of $Re_2H_8(dmpm)_2$ with dmpm in the presence of $HBF_4{\cdot}Et_2O$ (eq 4) or, alternatively, through a one-pot synthesis involving the reaction of $Re_2Cl_4(dmpm)_3$ with $LiAlH_4$ in THF followed by hydrolysis with aqueous THF and subsequent reaction with KPF_6 (eq 5). Use of $NaBPh_4$ in place of KPF_6 gives $[Re_2H_5(dmpm)_3]BPh_4$. Prior to the addition of KPF_6 in eq 5, the $[Re_2H_5(dmpm)_3]^+$ cation is probably stabilized by some sort of aluminate anion (as yet unidentified); it shows intense broad

$$Re_2H_8(dmpm)_2 + dmpm + HBF_4 \rightarrow [Re_2H_5(dmpm)_3]BF_4 + 2H_2 \quad (4)$$

$$Re_2Cl_4(dmpm)_3 + LiAlH_4 \xrightarrow[(2)\,KPF_6/H_2O]{(1)\,THF/H_2O} [Re_2H_5(dmpm)_3]PF_6 \quad (5)$$

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(33) Ebner, J. R.; Walton, R. A. *Inorg. Chem.* **1975**, *14*, 1987.

ν(OH) bands at 3362 and 3266 (sh) cm^{-1} and δ(OH) at 1638 cm^{-1} in the IR spectrum. These bands disappear upon formation of the PF_6^- salt. The ^1H and ^{31}P NMR spectral properties of the cation pre and post PF_6^- exchange are identical. The reaction in eq 5 is readily adapted to the preparation of $[Re_2D_5(dmpm)_3]PF_6$.

The electrochemical and spectroscopic properties of $[Re_2H_5(dmpm)_3]BF_4$ are identical to those of the PF_6^- salt except for a ν(B–F) mode at 1060 (s) cm^{-1} in the IR spectrum of the former complex. The IR spectra of both salts show several fairly intense ν(Re–H) modes between 2100 and 1800 cm^{-1} (Table VIII). These are absent in the spectrum of $[Re_2D_5(dmpm)_3]PF_6$, which shows ν(Re–D) bands overlapping the δ(C–H) modes of the dmpm ligands between 1500 and 1300 cm^{-1}. The more important properties of $[Re_2H_5(dmpm)_3]PF_6$ are summarized in Table VIII. A solution of this salt in acetone gave a conductivity characteristic of a 1:1 electrolyte in this solvent (Λ_m = 105 Ω^{-1} cm^2 mol^{-1}).

The electrochemical properties of $[Re_2H_5(dmpm)_3]PF_6$, studied by cyclic voltammetry, are unlike those of other dirhenium pentahydrides studied previously[12b,14] as well as the complexes $[Re_2H_5(dppe)_3]BF_4$, $[Re_2H_5(dppe)_2(dppm)]BF_4$, and $[Re_2H_5(PMe_3)_4(LL)]PF_6$ (LL = dppe, dppm) (see Table VIII). These have much more accessible oxidations than does $[Re_2H_5(dmpm)_3]PF_6$ (compare, for example, the data in Table VIII). A solution of $[Re_2H_5(dmpm)_3]PF_6$ in 0.1 M TBAH/CH_2Cl_2 displays two irreversible oxidations at $E_{p,a}$ = +0.62 and +0.94 V in its cyclic voltammogram. The first oxidation is much more positive than the $E_{1/2}$(ox) value for $[Re_2H_5(dppe)_3]BF_4$. At first sight, this is contrary to what one would expect, since increased phosphine basicity (dmpm > dppe) should lead to a negative shift in this potential. Accordingly, this result is in accord with a major structural difference between $[Re_2H_5(dppe)_3]^+$ and $[Re_2H_5(dmpm)_3]^+$, as we have found to be the case.

The complex $[Re_2H_5(dmpm)_3]PF_6$ has an uncomplicated ^1H NMR spectrum; the methyl resonance appears as a singlet at δ +1.82, while the broad methylene resonance at δ +2.98 resembles a poorly resolved triplet. A binomial septet occurs at δ −8.42 ($^2J_{PH}$ = 9.2 Hz) due to the hydrides being coupled to six equivalent phosphorus atoms. The simplicity of the spectrum reflects the occurrence of a fluxional process that renders the hydride ligands equivalent on the NMR time scale. This hydride resonance is observed to broaden upon lowering the temperature from +20 to −80 °C but is otherwise unchanged, and we were unable to obtain the spectrum of the limiting static structure. Likewise, the P–CH_3 resonance broadened slightly but otherwise remained unchanged as the temperature was lowered. A quite remarkable property of the $[Re_2H_5(dmpm)_3]^+$ cation is its solubility in water; such solutions are stable in air for extended periods. A very simple ^1H NMR spectrum is obtained in D_2O. Two singlets are located at δ +3.0 (br) and +1.7 which are assigned to the methylene and methyl protons of the dmpm ligands, respectively. The hydride resonance appears as a septet at −8.3 ($^2J_{PH}$ = 9.0 Hz). The intensity of this signal slowly decreases as the hydride ligands exchange with deuterium of the solvent. The $^{31}P\{^1H\}$ spectrum in CD_2Cl_2 displays a singlet at δ −28.7 corresponding to the dmpm phosphorus atoms. Also, a binomial septet is observed at δ −143.4 for the PF_6^- anion. A selective 2DJ ^{31}P NMR experiment was used to confirm the number of hydride ligands present; the phosphorus resonance is split into six peaks ($^2J_{PH}$ = 9.2 Hz).

The single-crystal X-ray structure of $[Re_2H_5(dmpm)_3]PF_6$ showed the solid-state structure of the cation to be $[Re_2(\mu\text{-}H)H_4(\mu\text{-}dmpm)_3]^+$ (Figure 4). The key structural parameters of the cation are listed in Table VII.

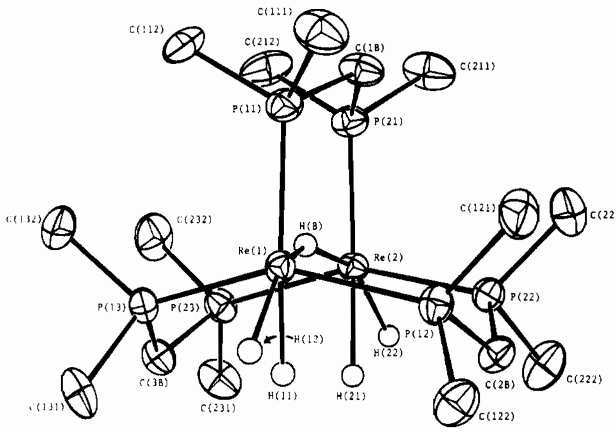
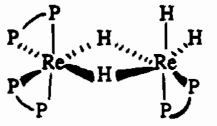


Figure 4. ORTEP view of the rhenium-containing cation of 3 with the hydrogen atoms of the dmpm ligands omitted. The thermal ellipsoids are drawn at the 50% probability level except for the hydride ligands, which are circles of arbitrary radii.

Discussion

(a) Complexes Containing 1,2-Bis(diphenylphosphino)ethane and Bis(diphenylphosphino)methane. The isolation of the pairs $Re_2H_4(dppe)_2(LL)$ and $[Re_2H_5(dppe)_2(LL)]BF_4$ (LL = dppe, dppm), along with $Re_2H_4(PMe_3)_4(dppe)$ and $[Re_2H_5(PMe_3)_4(dppe)]X$ (X = BF_4, PF_6), provides the only examples, other than $Re_2H_4(PMe_2Ph)_4[P(OCH_2)_3CEt]_2$ and $\{Re_2H_5(PMe_2Ph)_4[P(OCH_2)_3CEt]_2\}BF_4$,[20] of dirhenium tetrahydride/pentahydride conjugate pairs. The system studied by Green et al.[20] differs from ours in containing only monodentate phosphine/phosphite ligands. This pair of complexes[20] contains three bridging and one or two terminal hydride ligands, which is not always the case with the complexes prepared by us. The complex $Re_2H_4(dppe)_3$ has ^1H and $^{31}P\{^1H\}$ NMR spectra that accord with the presence of two bridging and two terminal hydride ligands and with three pairs of inequivalent phosphorus atoms in chelating dppe ligands. These characteristics are best accommodated in structure I. In contrast to this situation, the NMR spectral properties of $Re_2H_4(dppe)_2(dppm)$ support the presence of three bridging and one terminal hydride ligands and two chelating dppe and one bridging dppm ligands (structure II). Both complexes display a reversible one-electron oxidation in their cyclic voltammograms at very negative potentials ($E_{1/2}$(ox) = ca. −0.55 V). Not only does this reflect their sensitivity to oxidation, but since it is also an indication of the electron-rich character of the low valent metal centers, it also accords with their strong basicity and ease of protonation (vide infra).



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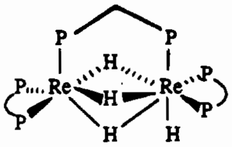

II

In earlier studies[14,15] of the reaction of PMe_3 with $Re_2H_8(PMe_3)_4$, it was found that the reaction course was solvent dependent; in benzene the reaction affords $Re_2H_6(PMe_3)_5$ whereas the $[Re_2H_5(PMe_3)_6]^+$ cation is formed in methanol, a protonating solvent. The highly basic, and presumably very unstable, tetrahydride $Re_2H_4(PMe_3)_6$ could not be obtained. In contrast, $Re_2H_8(dppe)_2$ reacts with dppe to give $Re_2H_4(dppe)_3$ when either benzene or methanol is used as the reaction solvent.

The protonation of $Re_2H_4(dppe)_3$ gives the pentahydride dirhenium cation whose distribution of hydride ligands is symmetrical but whose formation is accompanied by a switch of one of the chelating dppe ligands from a chelating to an intramolecular bridging mode. This is not only supported by NMR spectroscopy but also confirmed by an X-ray crystal structure of the $[Re_2H_5(dppe)_3]^+$ cation in its perrhenate salt (Figure 2). This complex was obtained, along with $[ReO_2(dppe)_2]ReO_4$, during an unsuccessful attempt to grow crystals of $Re_2H_8(dppe)_2$.

Apparently, a portion of $Re_2H_8(dppe)_2$ decomposed with release of dppe, which then reacted with some of the remaining $Re_2H_8(dppe)_2$ to produce $Re_2H_4(dppe)_3$, which in turn became protonated in the THF/methanol solvent system.[27] The formation of the ReO_4^- counterion is attributed to the slow diffusion of some oxygen into the system during the prolonged period over which these reactions and subsequent crystal growth occurred. However, the oxygen-containing THF and methanol solvents could also play a role in the oxygenation reactions. The presence of $[ReO_2(dppe)_2]ReO_4$ is most likely the result of a separate decomposition pathway, since the $[Re_2H_5(dppe)_3]^+$ cation seems to be fairly stable to low levels of O_2 and does not convert to $[ReO_2(dppe)_2]^+$. The complex $[Re_2H_5(dppe)_3]ReO_4$ is isostructural with $[Re_2H_5(dppe)_3]BF_4$, and the dirhenium cation has been shown to have the structure $[(dppe)HRe(\mu\text{-}H)_3(\mu\text{-}dppe)ReH(dppe)]^+$. While we did not locate the hydride ligands in this structure determination, the presence of three bridging hydride ligands and one terminal hydride per rhenium atom is compatible with the geometry of the Re_2P_6 skeleton and the ^1H NMR spectral results (Table VIII and Figure 1). In the solid state this structure is rather unsymmetrical, since the two chelate rings exhibit different conformations. The ring formed at Re(2) has an "envelope"-type puckering of a kind encountered previously with dimetal complexes that contain dppe and related bidentate phosphine ligands.[34] The P–C–C–P unit is almost planar (the torsional angle P(22)–C(223)–C(233)–P(23) is ca. 5 (2)°). The ring at Re(1) is much more puckered, as shown by the P(13)–C(133)–C(123)–P(12) torsional angle of ca. 49 (1)°. The unsymmetric nature of the Re_2P_6 core is also reflected in the disparity in the P–Re–Re–P torsional angles, which in the case of P(11)–Re(1)–Re(2)–P(21), P(12)–Re(1)–Re(2)–P(23), and P(13)–Re(1)–Re(2)–P(22) are 8.0 (1), 47.9 (2), and 50.9 (2)°, respectively. The presence of three separate phosphorus signals in the $^{31}P\{^1H\}$ NMR spectrum at –40 °C is also consistent with this low-symmetry structure. The Re–Re distance of 2.576 (1) Å in the $[Re_2H_5(dppe)_3]^+$ cation is a little shorter than those distances reported for the analogous phosphite $\{Re_2H_5(PMe_2Ph)_4[P(OCH_2)_3CEt]_2\}^+$ (2.605 (2) Å)[20] and isocyanide $[Re_2H_5(PPh_3)_4(CN\text{-}t\text{-}Bu)_2]^+$ (2.604 (1) Å)[16] complexes but is characteristic of hydrido-bridged dirhenium complexes that contain three or four bridging hydride ligands.[2a,9,10,15,16,20,35] The average Re–P distance of 2.359 (3) Å is also consistent with those found in these related structures.[16,20] There are no obvious differences between the Re–P distances associated with the three chemically different dppe ligands.

The complex $[ReO_2(dppe)_2]ReO_4$ (**2**) has a structure similar to those of other complexes that contain the trans $[O{=}Re{=}O]^+$ moiety[36] and merits little further discussion. The Re–O distances of 1.781 (6) Å are typical for a *trans*-dioxo species and agree well with the value of 1.79 (2) Å reported for $[ReO_2(PMe_3)_4]ReO_4$.[37] The Re–P distances (2.497 (3) and 2.485 (3) Å) are also in good agreement with those in $[ReO_2(PMe_3)_4]ReO_4$ (2.485 (8) Å).[37]

The protonation of $Re_2H_4(dppe)_2(dppm)$ to give $[Re_2H_5(dppe)_2(dppm)]BF_4$ differs from the corresponding protonation of $Re_2H_4(dppe)_3$ in that the former reaction does not appear to be accompanied by any change in the bonding modes of the phosphine ligands (as measured by $^{31}P\{^1H\}$ NMR spectroscopy); i.e., the Re_2P_6 skeleton remains as $(dppe)Re(\mu\text{-}dppm)Re(dppe)$. While the ^1H NMR spectrum of this complex accords with a fluxional process that renders the hydride ligands equivalent at room temperature, the similarity of the cyclic voltammetric properties of this complex to those of $[Re_2H_5(dppe)_3]BF_4$ (Table VIII) and other pentahydridodirhenium cations,[12b,14] which possess limiting static structures with three bridging and two terminal hydride ligands, implies that this mixed dppe–dppm complex cation has the structure $[(dppe)HRe(\mu\text{-}H)_3(\mu\text{-}dppm)ReH(dppe)]^+$.

In accord with the structure change that accompanies the protonation of $Re_2H_4(dppe)_3$, we note that the pentahydride cation cannot be deprotonated by DBU, whereas $[Re_2H_5(dppe)_2(dppm)]BF_4$ can be reconverted to $Re_2H_4(dppe)_2(dppm)$ by this reagent. Reversible protonation/deprotonation reactions have been observed previously for the dinuclear rhenium polyhydrides $Re_2H_8(PR_3)_4$ ($PR_3 = PPh_3$,[13] PMe_3[14]). However, the deprotonation of $[Re_2H_9(PR_3)_4]^+$ is accessible through use of the weaker base NEt_3.[13,14] The fact that a stronger base is required for the deprotonation of $[Re_2H_5(dppe)_2(dppm)]BF_4$ gives an indication of the greater basicity of the tetrahydride complex $Re_2H_4(dppe)_2(dppm)$ compared to $Re_2H_8(PR_3)_4$.

The conversion of one of the chelating dppe ligands in $Re_2H_4(dppe)_3$ to an *intramolecular* bridging mode is unusual but is not without precedent. Thus, the important isomerization process that leads to the conversion of multiply bonded complexes of the type $\alpha\text{-}M_2X_4(dppe)_2$ (M = Mo, W; X = Cl, Br) to $\beta\text{-}M_2X_4(dppe)_2$ involves a switch in the bonding mode of *both* dppe ligands from chelating to bridging, with an associated change in rotational geometry about the M–M bond from eclipsed to staggered.[38,39]

While $^{31}P\{^1H\}$ NMR spectroscopy showed that the product from the reaction between $Re_2H_8(dppe)_2$ and PMe_3 is impure, the isolated solid probably contains $Re_2H_4(dppe)_2(PMe_3)_2$ as a major component. This is supported by its cyclic voltammogram (recorded on a solution in 0.1 M TBAH/CH_2Cl_2) which shows $E_{1/2}(ox) = -0.69$ V vs Ag/AgCl, a value intermediate between the corresponding $E_{1/2}(ox)$ values for $Re_2H_4(dppe)_3$ and $Re_2H_4(PMe_3)_4(dppe)$, which are –0.54 and –0.81 V, respectively (Table VIII). The latter compound, which is prepared by the reaction of $Re_2H_8(PMe_3)_4$ with dppe, is the closest we have yet to come to preparing $Re_2H_4(PMe_3)_6$. On the basis of the $E_{1/2}(ox)$ values for $Re_2H_6(PMe_3)_5$ and $Re_2H_4(PMe_3)_4(dppe)$ of –0.79[15] and –0.81 V (Table VIII), we would expect $Re_2H_4(PMe_3)_6$ to be even more susceptible to oxidation and therefore exceedingly difficult to isolate. The much greater stability of $[Re_2H_5(PMe_3)_6]^+$ is thus readily understandable.[14,15]

The ease of protonating $Re_2H_4(PMe_3)_4(dppe)$ to give $[Re_2H_5(PMe_3)_4(dppe)]BF_4$ is also in accord with these results, as is the isolation of $[Re_2H_5(PMe_3)_4(LL)]PF_6$ (LL = dppe, dppm) from the reactions of $Re_2H_8(PMe_3)_4$ with a mixture of the ligand LL and KPF_6 in methanol. The latter reactions almost certainly involve the protonation of neutral dirhenium polyhydride intermediates by the methanol solvent;[15] detailed mechanistic studies are not planned.

The room-temperature ^1H NMR spectra of $Re_2H_4(PMe_3)_4(dppe)$ and $[Re_2H_5(PMe_3)_4(LL)]PF_6$ show broad singlets for the Re–*H* resonances, which indicates that the hydride ligands are rendered equivalent by a fluxional process. A relatively rigid Re_2P_6 skeleton is in accord with the $^{31}P\{^1H\}$ NMR spectra, which are consistent with the ligand disposition $(dppe)(Me_3P)ReRe(PMe_3)_3$ for both $Re_2H_4(PMe_3)_4(dppe)$ and $[Re_2H_5(PMe_3)_4(dppe)]^+$ and the more symmetrical structure $(Me_3P)_2Re(\mu\text{-}dppm)Re(PMe_3)_2$ for $[Re_2H_5(PMe_3)_4(dppm)]^+$.

(b) Complexes Containing Bis(dimethylphosphino)methane.

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[34] See, for example: Bakir, M.; Cotton, F. A.; Falvello, L. R.; Vidyasagar, K.; Walton, R. A. *Inorg. Chem.* **1988**, *27*, 2460.

[35] Abrahams, S. C.; Ginsberg, A. P.; Koetzle, T. F.; Marsh, P.; Sprinkle, C. R. *Inorg. Chem.* **1986**, *25*, 2500.

[36] Conner, K. A.; Walton, R. A. *Comprehensive Coordination Chemistry*; Pergamon: Oxford, England, 1987; Chapter 43, pp 185–187.

[37] Edwards, P. G.; Skapski, A. C.; Slawin, A. M. Z.; Wilkinson, G. *Polyhedron* **1984**, *3*, 1083.

[38] (a) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982. (b) Cotton, F. A.; Walton, R. A. *Struct. Bonding (Berlin)* **1985**, *62*, 1.

[39] (a) Best, S. A.; Smith, T. J.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 99. (b) Schrock, R. R.; Sturgeoff, L. G.; Sharp, P. R. *Inorg. Chem.* **1983**, *22*, 2801. (c) Agaskar, P. A.; Cotton, F. A. *Inorg. Chem.* **1984**, *23*, 3383. (d) Cole, N. F.; Derringer, D. R.; Fiore, E. A.; Knoechel, D. J.; Schmitt, R. K.; Smith, T. J. *Inorg. Chem.* **1985**, *24*, 1978. (e) Agaskar, P. A.; Cotton, F. A.; Derringer, D. R.; Powell, G. L.; Root, D. R.; Smith, T. J. *Inorg. Chem.* **1985**, *24*, 2786. (f) Agaskar, P. A.; Cotton, F. A. *Inorg. Chem.* **1986**, *25*, 15.

The cationic complex $[Re_2H_5(dmpm)_3]^+$ can be isolated as its BF_4^- and PF_6^- salts by two separate routes (eqs 4 and 5). Its properties show that it is different structurally from all other known pentahydridodirhenium cations in both solution and the solid state. The cyclic voltammogram of a solution of $[Re_2H_5(dmpm)_3]PF_6$ shows two irreversible oxidations ($E_{p,a}$ = +0.62 and +0.94 V), whereas all other species of the type $[Re_2H_5(PR_3)_6]^+$ possess two oxidations that are separated by ca. 0.8 V, the first of which is reversible with $E_{1/2}(ox)$ in the range −0.11 to +0.36 V, the actual value being dependent upon the nature of the ancillary ligands (see refs 12b and 14 and Table VIII).

The simplicity of the NMR spectra down to −80 °C signifies the existence of a fluxional process (or processes) that renders the hydride ligands and phosphorus atoms equivalent. A comparison of the $^{31}P\{^1H\}$ NMR spectra of the pair of complexes $Re_2H_8(PMe_3)_4$ (δ −25.9)[7] and $[Re_2H_5(PMe_3)_6]^+$ (δ −31.3),[14] which like their dmpm analogues are also fluxional in solution, shows that the chemical shift difference is quite small (ca. 5.4 ppm) whereas between $Re_2H_8(dmpm)_2$ (δ +6.2) and $[Re_2H_5(dmpm)_3]^+$ (δ −28.7) the corresponding upfield shift is ca. 35 ppm. Along with the electrochemical results, this implies that $[Re_2H_5(dmpm)_3]^+$ may be structurally quite different from the other pentahydridodirhenium cations. This is confirmed by the X-ray crystal structure of $[Re_2H_5(dmpm)_3]PF_6$.

The structure of the $[Re_2H_5(dmpm)_3]^+$ cation, which is shown in Figure 4, can be represented as $[Re_2(\mu\text{-}H)H_4(\mu\text{-}dmpm)_3]^+$. While this species possesses no crystallographically imposed symmetry, it approximates to C_{2v} symmetry with the mirror plane encompassing the carbon atoms of the CH_2 groups of the three dmpm ligands and bisecting the Re–Re vector. The Re_2P_6 skeleton is essentially eclipsed with P–Re–Re–P torsional angles close to zero. This is in contrast to the chloride complex $Re_2Cl_4(\mu\text{-}dmpm)_3$, which also contains three bridging dmpm ligands, where the torsional angles are ca. 30°.[22] The most remarkable feature in this hydride structure is the very long Re···Re distance of 3.5150 (4) Å, which clearly accords with the absence of any direct Re–Re bonding. We can view the structure as arising formally from the protonation of the neutral species $Re_2H_4(dmpm)_3$, in which the individual Re atoms have 15-electron counts, such that a 3-center, 2-electron Re–H–Re bonding interaction gives rise to a diamagnetic ground state. This structure differs from those of all other $[Re_2H_5]^+$ species that have been structurally characterized, including $[Re_2H_5(dppe)_3]^+$,[16,20,21a] in which there is a $[HRe(\mu\text{-}H)_3ReH]$ unit and a very short Re–Re distance (2.58–2.60 Å). This structure of $[Re_2H_5(dmpm)_3]^+$ may represent one structural extreme in the series of terminal/bridging Re–H bond forming/breaking processes that presumably account for the fluxionality of this complex in solution.

The two Re–P distances which are trans to terminal Re–H bonds are slightly longer (average 2.406 [2] Å) than the set that are essentially trans to one another (average 2.370 [9] Å). The terminal Re–H bond lengths (1.6–1.8 (1) Å) are normal for M–H distances determined by X-ray crystallography;[40] the H···H distances are long (ca. 1.7 Å) and support this being a classical hydride structure. The apparent disparity in the measured Re–H(B) distances (1.53 (7) and 2.06 (7) Å), while greater than 3σ, is not considered to be significant in view of the difficulty of determining H atom positions in the presence of heavy metals by X-ray diffraction. However, if this difference in distances was real, it could be considered as evidence for a structure in which the two Re atoms had different electron counts, i.e., 14-electron and 16-electron. In this event, the species would show some resemblance to the unsymmetrical complex $(Me_2NH)(CO)_4Re(\mu\text{-}H)Re(CO)_4Cl$, which is formally composed of 18-electron and 16-electron fragments.[41]

The structural characterization of dirhenium polyhydrides that contain three or four bridging hydride ligands has revealed that in all cases the Re–Re distance is very short (2.51–2.61 Å).[2a,9,10,16,20,21a,35] This observation has led to the conclusion that some degree of multiple metal–metal bonding is present, represented in terms of direct Re–Re bonding and/or 3-center, 2-electron Re–H–Re bonds.[42,43] An important exception is the complex $Re_2(\mu\text{-}H)_2H_6(\mu\text{-}dppm)_2$ (dppm = $Ph_2PCH_2PPh_2$), which contains only two bridging hydride ligands and possesses a much longer Re–Re bond distance of 2.9335 (9) Å. The $[Re_2(\mu\text{-}H)H_4(\mu\text{-}dmpm)_3]^+$ cation takes this trend to its extreme, namely, no direct Re–Re interaction whatsoever and metal centers that are electronically unsaturated. This is an unusual result for a low-valent metal that normally show a propensity to form strong metal–metal interactions.[38] In spite of its electronic unsaturation, this complex has the remarkable property of being stable in air and water. However, we do find[44] that under thermal conditions it reacts with the π-acceptor CO and isocyanide ligands to give lower valent dirhenium complexes in which the $[Re_2(\mu\text{-}H)(\mu\text{-}dmpm)_3]$ unit is retained. These studies will be described in a separate report.

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Supplementary Material Available: Tables giving full details of the crystal data and data collection parameters (Tables S1–S3), atomic positional parameters (Tables S4–S7), anisotropic thermal parameters (Tables S8–S10), and complete bond distances (Tables S11–S13) and bond angles (Tables S14–S16) for **1**–**3** and figures showing the structures and atomic numbering schemes for **1** and **2** (Figures S1 and S2) (41 pages). Ordering information is given on any current masthead page.

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(40) Cotton, F. A.; Luck, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 5757.
(41) Adams, R. D.; Kuhns, J. D. *Polyhedron* **1988**, *7*, 2543.
(42) Dedieu, A.; Albright, T. A.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3141.
(43) Dahl, L. F. *Ann. N.Y. Acad. Sci.* **1983**, *415*, 1.
(44) Meyer, K. E.; Fanwick, P. E.; Walton, R. A. Unpublished results.