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Rhenium Polyhydride Complexes That Contain the Tripodal Phosphine CH₃C(CH₂PPh₂)₃ (triphos)

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The compound ReCl₃(triphos) (triphos = CH₃C(CH₂PPh₂)₃) reacts with NaBH₄ in ethanol to afford the pentahydrido complex ReH₅(triphos), which when treated with HBF₄·Et₂O in RCN (R = Me, Et) converts to [ReH(NCR)₃(triphos)](BF₄)₂. The direct reaction of ReH₅(triphos) with EPh₃ (E = P, As, Sb), dppe (Ph₂PCH₂CH₂PPh₂), and arphos (Ph₂PCH₂CH₂AsPh₂) produces the trihydrides ReH₃(triphos)(EPh₃), ReH₃(triphos)(η¹-dppe), and ReH₃(triphos)(η¹-arphos), respectively, the latter complex existing as a mixture of linkage isomers ReH₃(triphos)(arphos-*P*) and ReH₃(triphos)(arphos-*As*). A more convenient and higher yield preparation of the compounds ReH₃(triphos)L involves the direct reaction of ReCl₃(triphos) with NaBH₄ and EPh₃, dppe, or arphos. The trihydrides can be protonated by HBF₄·Et₂O to produce [ReH₄(triphos)L]BF₄, which are in turn readily deprotonated by NEt₃. In the absence of ligand L, solutions of ReH₅(triphos) evolve H₂ and the dark red dinuclear complex Re₂H₄(triphos)₂ is formed cleanly. It is very easily oxidized ($E_{1/2}$(ox) = -0.55 V vs Ag/AgCl in 0.1 M TBAH–CH₂Cl₂) to the green monocation [Re₂H₄(triphos)₂]⁺. Single-crystal X-ray structure determinations have been carried out on the compounds *fac*-ReCl₃(triphos) (1) and [Re₂H₄(triphos)₂]ReO₄·5C₆H₆ (2). Crystal data for 1 at 20 °C: orthorhombic space group *Pna*2₁, a = 17.332 (5) Å, b = 12.032 (3) Å, c = 17.542 (4) Å, V = 3658 (3) Å³, and Z = 4. The structure was refined to R = 0.039 (R_w = 0.047) for 1812 data with $I > 3\sigma(I)$. Crystal data for 2 at -61 °C: monoclinic space group *P*2₁/*n*, a = 16.765 (2) Å, b = 23.065 (3) Å, c = 25.109 (4) Å, β = 98.38 (1)°, V = 9605 (4) Å³, and Z = 4. The structure was refined to R = 0.028 (R_w = 0.035) for 9496 data with $I > 3.0\sigma(I)$. The structure of the cation can be represented as [(triphos)HRe(μ-H)₃Re(triphos)]⁺. Although the terminally bound hydride ligand was not located in this structure determination, its position can be inferred from the angular distortions that are present about one of the Re atoms. The Re–Re distance of 2.5389 (4) Å is typical of a mixed polyhydride–phosphine complex of dirhenium in which there are three or four bridging hydride ligands present.

Introduction

While an extensive chemistry has developed for rhenium polyhydride complexes that contain monodentate and bidentate phosphine ligands,[2] related species with tri- and tetradentate phosphines are scarce. Very recent reports have appeared on the use of PhP(CH₂CH₂CH₂PCy₂)₂[3] and PhP(CH₂CH₂PPh₂)₂[4] to stabilize the rhenium pentahydride fragment, ligands which would be expected to favor a meridional coordination in a six-coordinate octahedral complex i.e. *mer*-ReX₃(P₃). However, as far as we are aware, a tripodal ligand such as CH₃C(CH₂PPh₂)₃ (1,1,1-tris((diphenylphosphino)methyl)ethane; abbreviated triphos), which would favor a *fac*-ReX₃(P₃) stereochemistry, has not previously been employed in coordinating mononuclear rhenium polyhydrides although it has been instrumental in the stabilization of the dirhenium unit in the novel unsymmetrical complex Et₄N[Re₂(μ-H)₃H₆(triphos)].[5] We have recently developed a synthesis of the mononuclear complex ReH₅(triphos) and in the present report provide details of its properties and reactions with various phosphine, arsine, and stibine ligands.

Experimental Section

Starting Materials. The complexes ReCl₃(PPh₃)₂(NCCH₃)[6] and ReCl₃(triphos)[7] were prepared according to literature methods. The ligands 1,1,1-tris((diphenylphosphino)methyl)ethane (triphos) and bis-(2-(diphenylphosphino)ethyl)phenylphosphine (PP₂) were purchased from Strem Chemicals Inc. The complex ReCl₃(PP₂) was prepared by a procedure similar to that used[7] to obtain ReCl₃(triphos). A mixture of ReCl₃(PPh₃)₂(NCCH₃) (0.302 g, 0.352 mmol) and PP₂ (0.209 g, 0.391 mmol) was refluxed in 15 mL of benzene for 24 h. The light green precipitate was filtered off, washed with benzene (3 × 15 mL) and ethanol (2 × 15 mL), and dried under vacuum; yield 0.178 g (59%). Anal. Calcd for C₃₆H₃₅Cl₃P₃Re (i.e., ReCl₃[PhP(CH₂CH₂PPh₂)₂]·¹/₃C₆H₆): C, 50.68; H, 4.13. Found: C, 50.35; H, 4.37. The presence

(1) (a) Department of Chemistry. (b) Department of Medicinal Chemistry.
(2) See, for example: (a) Hlatky, G. G.; Crabtree, R. H. *Coord. Chem. Rev.* **1985**, *65*, 1 and references cited therein. (b) Conner, K. A.; Walton, R. A. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, England, 1987; Chapter 43 and references cited therein.
(3) Kim, Y.; Deng, H.; Meek, D. W.; Wojcicki, A. *J. Am. Chem. Soc.* **1990**, *112*, 2798.
(4) Luo, X.-L.; Crabtree, R. H. *J. Chem. Soc., Dalton Trans.* **1991**, 587.
(5) Abrahams, A. C.; Ginsberg, A. P.; Koetzle, T. F.; Marsh, P.; Sprinkle, C. R. *Inorg. Chem.* **1986**, *25*, 2500.
(6) Rouschias, G.; Wilkinson, G. *J. Chem. Soc. A* **1967**, 993.
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of lattice benzene was confirmed by ¹H NMR spectroscopy.

Solvents and other reagents were obtained from commercial sources and used without further purification. All solvents were deoxygenated with dinitrogen gas prior to use.

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

A. Synthesis of [ReCl₃(triphos)]NO₃. A quantity of ReCl₃(triphos) (0.120 g, 0.131 mmol) was stirred in 50 mL of concentrated HNO₃(aq) for 1 h. The resulting red precipitate was filtered off, washed with diethyl ether (3 × 15 mL), and dried under vacuum; yield 0.113 g (88%). Anal. Calcd for C₄₁H₄₄Cl₃NO₅.₅P₃Re (i.e., [ReCl₃(triphos)]NO₃·⁵/₂H₂O): C, 48.08; H, 4.33. Found: C, 48.06; H, 4.12.

B. Synthesis of ReH₅L₃ (L₃ = triphos, PP₂). **(i) ReH₅(triphos).** A mixture of ReCl₃(triphos) (0.123 g, 0.134 mmol) and NaBH₄ (0.123 g, 3.25 mmol) was refluxed in 15 mL of ethanol for 15 min. The light yellow precipitate was filtered off, washed with ethanol (2 × 15 mL) and methanol (3 × 15 mL), and dried under vacuum; yield 0.067 g (60%). Anal. Calcd for C₄₁H₄₇O₁.₅P₃Re (i.e., ReH₅(triphos)·³/₂H₂O): C, 58.42; H, 5.62. Found: C, 58.02; H, 5.37. The presence of water was substantiated by the IR spectrum of this product (Nujol mull), which showed *ν*(OH) at 3350 m, br cm⁻¹ and δ(OH) ca. 1650 w, cm⁻¹.

(ii) ReH₅(PP₂). This compound was prepared from ReCl₃(PP₂) by a procedure similar to that described in section B(i); yield 60%.

C. Protonation Reactions of ReH₅L₃. **(i) [ReH₆(PP₂)]BF₄.** A quantity of ReH₅(PP₂) (0.070 g, 0.097 mmol) was admixed with 10 mL of benzene and 0.2 mL of 85% HBF₄·Et₂O. Diethyl ether (75 mL) was added after 30 min of stirring to precipitate a light yellow solid. The solid was filtered off, washed with diethyl ether (3 × 15 mL), and dried under vacuum; yield 0.077 g (98%).

Attempts to convert ReH₅(triphos) to [ReH₆(triphos)]BF₄ by such a procedure were unsuccessful. In all instances these reactions led to decomposition and the formation of unidentified products.

(ii) [ReH(NCCH₃)₃(triphos)](BF₄)₂. A quantity of ReH₅(triphos) (0.060 g, 0.074 mmol) was allowed to react with 85% HBF₄·Et₂O (0.1 mL) in 5 mL of acetonitrile. After the mixture had been stirred for 30 min, 60 mL of diethyl ether was added to induce precipitation of an orange solid. The crude product was filtered off and recrystallized from CH₂Cl₂ (10 mL)/diethyl ether (50 mL); yield 0.055 g (53%). Anal. Calcd for C₄₇H₄₉Br₂F₈P₃Re: C, 50.92; H, 4.45. Found: C, 48.76; H, 4.54. We obtained consistently low carbon microanalyses for this complex, which may reflect the presence of a small amount of BF₄⁻-containing contaminant that we were unable to remove. However, the spectroscopic and electrochemical properties of this product gave no hint of contamination by any other species.

(iii) [ReH(NCEt)₃(triphos)](BF₄)₂. This complex was obtained in 56% yield by a procedure similar to that described in section C(ii).

D. Synthesis of ReH₃(triphos)(EPh₃) (E = P, As, Sb). **(i) ReH₃-(triphos)(PPh₃).** A mixture of ReCl₃(triphos) (0.061 g, 0.067 mmol),

PPh$_3$ (0.092 g, 0.351 mmol), and NaBH$_4$ (0.054 g, 1.42 mmol) was refluxed in 15 mL of ethanol for 1 h. The orange precipitate was filtered off, washed with ethanol (2 × 15 mL) and methanol (2 × 15 mL), and dried under vacuum; yield 0.042 g (58%). Anal. Calcd for C$_{59}$H$_{59}$OP$_4$Re (i.e., ReH$_3$(triphos)(PPh$_3$)·H$_2$O): C, 64.76; H, 5.43. Found: C, 64.56; H, 5.37.

Similar procedures were used to prepare the analogous AsPh$_3$ and SbPh$_3$ derivatives, the identities of which were established from their spectroscopic and electrochemical properties.

(ii) **ReH$_3$(triphos)(AsPh$_3$).** Yield: 62%.

(iii) **ReH$_3$(triphos)(SbPh$_3$).** Yield: 60%.

E. Protonation Reactions of ReH$_3$(triphos)(EPh$_3$). (i) **[ReH$_4$(triphos)(PPh$_3$)]BF$_4$.** A quantity of ReH$_3$(triphos)(PPh$_3$) (0.235 g, 0.216 mmol) was placed in a solution of CH$_2$Cl$_2$ (10 mL) and 85% HBF$_4$·Et$_2$O (0.2 mL). After 60 min of stirring this reaction mixture, diethyl ether (100 mL) was added to induce precipitation of a white solid. The solid was filtered off, washed with diethyl ether (3 × 15 mL), and dried under vacuum; yield 0.113 g (45%). Anal. Calcd for C$_{59}$H$_{63}$BF$_4$O$_{2.5}$P$_4$Re (i.e., [ReH$_4$(triphos)(PPh$_3$)]BF$_4$·^{5}/$_2$H$_2$O): C, 58.61; H, 5.25. Found: C, 58.58; H, 5.11. The presence of lattice water was substantiated by the IR spectrum of this product (Nujol mull), which showed ν(OH) at 3350 m, br cm^{-1} and δ(OH) at ca. 1650 w cm^{-1}.

When this complex (ca. 0.05 g) is refluxed with a solution of NEt$_3$ (0.2 mL) in ethanol (5 mL) for 15 min, it deprotonates to re-form ReH$_3$-(triphos)(PPh$_3$) in near-quantitative yield. The resulting light yellow solid was filtered off, washed with ethanol (15 mL) and methanol (2 × 15 mL), and dried under vacuum.

(ii) **[ReH$_4$(triphos)(AsPh$_3$)]BF$_4$.** This complex (and its SbPh$_3$ analogue; vide infra) was prepared by the use of a procedure similar to that described in section E(i). Yield: 62%.

(iii) **[ReH$_4$(triphos)(SbPh$_3$)]BF$_4$.** Yield: 68%.

These two complexes can be deprotonated by NEt$_3$ in ethanol to regenerate the corresponding ReH$_3$(triphos)(EPh$_3$) compounds.

F. Synthesis of ReH$_3$(triphos)(η^1-LL) (LL = dppe, arphos). (i) **ReH$_3$(triphos)(η^1-dppe).** A mixture of ReCl$_3$(triphos) (0.100 g, 0.109 mmol), dppe (0.217 g, 0.545 mmol), and NaBH$_4$ (0.105 g, 2.78 mmol) was refluxed in ethanol for 2 h. The light yellow precipitate was filtered off, washed with ethanol (5 × 15 mL) and methanol (5 × 15 mL), and dried under vacuum; yield 0.080 g (60%). Anal. Calcd for C$_{67}$H$_{68}$OP$_5$Re (i.e. ReH$_3$(triphos)(dppe)·H$_2$O): C, 65.40; H, 5.57. Found: C, 65.44; H, 5.54. The presence of water of crystallization was supported by the IR spectrum of this product (Nujol mull), which showed ν(OH) at 3350 m, br cm^{-1} and δ(OH) at ca. 1650 w cm^{-1}.

The protonation of this complex to give [ReH$_4$(triphos)(η^1-dppe)]BF$_4$ and, in turn, the deprotonation of the tetrahydro cation by NEt$_3$ in ethanol were carried out through the use of the procedures described in section E(i).

(ii) **ReH$_3$(triphos)(η^1-arphos).** This complex was obtained with the use of a recipe similar to that described in section F(i). Yield: 47%. The product was found by NMR spectroscopy to be a mixture of linkage isomers (see under Results). Its protonation reactions were not examined.

G. Synthesis of Re$_2$H$_4$(triphos)$_2$. A mixture of ReCl$_3$(triphos) (0.118 g, 0.128 mmol) and NaBH$_4$ (0.115 g, 3.04 mmol) was refluxed in ethanol for 1 h. The resulting red precipitate was filtered off, washed with ethanol (2 × 15 mL), and dried under vacuum; yield 0.072 g (63%). We were unable to obtain satisfactory C and H microanalyses for this complex, in part because of its rapid oxidation to [Re$_2$H$_4$(triphos)$_2$]$^+$, which we were able to isolate as its perrhenate salt.

H. Synthesis of [Re$_2$H$_4$(triphos)$_2$]ReO$_4$. A mixture of Re$_2$H$_4$(triphos)$_2$ (0.028 g, 0.017 mmol) and C$_7$H$_7$PF$_6$ (0.007 g, 0.029 mmol) was stirred in 15 mL of CH$_2$Cl$_2$ for 30 min. The resulting green solution was evaporated to a viscous oil under a stream of N$_2$(g) and then triturated with diethyl ether (50 mL) to induce precipitation of a green solid. The solid was filtered off, washed with pentane (2 × 15 mL) and diethyl ether (2 × 15 mL), and dried under vacuum; yield 0.010 g (31%). Anal. Calcd for C$_{82}$H$_{84}$O$_5$P$_6$Re$_3$ (i.e. [Re$_2$H$_4$(triphos)$_2$]ReO$_4$·H$_2$O): C, 51.99; H, 4.47. Found: C, 51.90; H, 4.55. The presence of water was substantiated by the IR spectrum of this product (Nujol mull), which showed ν(OH) at 3350 m, br cm^{-1} and δ(OH) at ca. 1650 w cm^{-1}, as was the presence of [ReO$_4$]$^-$, which was confirmed by a strong ν(Re–O) mode at 912 cm^{-1}. The identity of the product was confirmed by a single-crystal X-ray structure analysis on a sample obtained by an entirely different procedure (vide infra).

Preparation of Single Crystals of ReCl$_3$(triphos) and [Re$_2$H$_4$(triphos)$_2$]ReO$_4$. Suitable crystals of ReCl$_3$(triphos) (1) were obtained by diffusion of pentane into a dichloromethane solution of this complex over a period of several days. A batch of dark red crystals of composition [Re$_2$H$_4$(triphos)$_2$]ReO$_4$·5C$_6$H$_6$ was obtained by allowing a solution of ReH$_5$(triphos) in deoxygenated benzene to stand for several weeks in the dark.

Table I. Crystallographic Data for ReCl$_3$(triphos) (**1**) and [Re$_2$H$_4$(triphos)$_2$]ReO$_4$·5C$_6$H$_6$ (**2**)

	1	2
chem formula	ReCl$_3$P$_3$C$_{41}$H$_{39}$	Re$_3$P$_6$O$_4$C$_{112}$H$_{112}$
fw	917.25	2266.59
space group	*Pna*2$_1$ (No. 33)	*P*2$_1$/*n* (No. 14)
a, Å	17.332 (5)	16.765 (2)
b, Å	12.032 (3)	23.065 (3)
c, Å	17.542 (4)	25.109 (4)
β, deg		98.33 (1)
V, Å^3	3658 (3)	9605 (4)
Z	4	4
T, °C	20	−61
λ, Å (Mo Kα)	0.710 73	0.710 73
ρ_{calcd}, g cm^{-3}	1.665	1.567
μ(Mo Kα), cm^{-1}	37.46	39.73
transm coeff	1.00–0.738	1.00–0.745
R^a	0.039	0.028
$R_w{}^b$	0.049	0.035

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

X-ray Structure Analyses. The structures of ReCl$_3$(triphos) (**1**) and [Re$_2$H$_4$(triphos)$_2$]ReO$_4$·5C$_6$H$_6$ (**2**) were determined by the application of standard procedures. The basic crystallographic parameters are listed in Table I. The cell constants are based on 25 reflections with 15 < θ < 19° for **1** and 21 < θ < 23° for **2**. Three standard reflections were measured after every 5000 s of beam exposure during data collection. Calculations were performed on a microVAX II computer using the Enraf-Nonius structure determination package. The crystal of **1** was found to belong to the orthorhombic space group *Pna*2$_1$ (No. 33), while **2** was monoclinic *P*2$_1$/*n* (No. 14). Lorentz and polarization corrections were applied to both sets of data. 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, including the carbon atoms of five independent molecules of benzene of crystallization in **2** which are located about general positions. Three bridging hydride ligands were tentatively located in the structure of **2** following anisotropic refinement of all non-hydrogen atoms (except for the carbon atoms of the benzenes of crystallization). Their refinement gave reasonable Re–H bond distances. An additional hydride ligand was not located in the structure of **2**, in spite of our expectation that one terminal Re–H bond is present (see under Results and Discussion). The positions of the hydrogen atoms of the triphos ligand of **1** and **2**, as well as the benzene lattice molecules of **2**, were calculated by assuming an 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. An empirical absorption correction was used in both cases,[8] the linear absorption coefficients being 37.46 cm^{-1} for **1** and 39.73 cm^{-1} for **2**. No corrections for extinction were applied.

The structures were refined in full-matrix least-squares, where the function minimized was $\sum w(|F_o| - |F_c|)^2$, where *w* is the weighting factor defined as $w = 1/\sigma^2(F_o)$. The non-hydrogen atoms were refined anisotropically with the exception of the phenyl group carbon atoms of **1** and the carbon atoms of the benzenes of crystallization of **2**; corrections for anomalous scattering were applied to all anisotropically refined atoms.[9] The largest peak in the final difference map of **1** was 1.29 e/Å^3, while for **2** the largest peak was 1.16 e/Å^3, but neither was at bonding distances to the rhenium atoms.

Positional parameters and their errors for all non-hydrogen atoms except the phenyl group atoms of **1** and the phenyl group atoms and benzenes of crystallization of **2** are listed in Tables II and III. Important intramolecular bond distances and angles are given in Tables IV and V. Tables giving full details of the crystal data and data collection parameters (Tables S1 and S2) and listings of all positional parameters (Tables S3–S6), thermal parameters (Tables S7 and S8), and complete bond distances (Tables S9 and S10) and bond angles (Tables S11 and S12)

(8) Flack, H. D. *Acta Crystallogr., Sect. A: Found Crystallogr.* **1977**, *A33*, 890.

(9) (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	0.15182 (3)	0.24511 (5)	0.25	2.238 (8)
Cl(1)	0.1643 (3)	0.0560 (4)	0.2935 (3)	4.1 (1)
Cl(2)	0.2279 (3)	0.1919 (5)	0.1469 (3)	4.2 (1)
Cl(3)	0.2686 (3)	0.2829 (4)	0.3197 (3)	3.8 (1)
P(1)	0.0274 (2)	0.2112 (4)	0.1916 (3)	2.18 (8)
P(2)	0.0746 (3)	0.3003 (4)	0.3649 (3)	2.46 (8)
P(3)	0.1355 (3)	0.4353 (4)	0.2098 (3)	2.37 (9)
C(10)	−0.0213 (8)	0.417 (1)	0.257 (1)	2.5 (3)
C(11)	−0.045 (1)	0.298 (2)	0.237 (1)	3.1 (4)
C(14)	−0.098 (1)	0.488 (2)	0.264 (1)	3.7 (4)
C(21)	0.013 (1)	0.422 (1)	0.341 (1)	3.0 (4)
C(31)	0.033 (1)	0.469 (1)	0.199 (1)	2.8 (4)

[a] *B* values for 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 and Non-Lattice Benzene Group Atoms of **2** and Their Estimated Standard Deviations[a]

atom	x	y	z	B
Re(1)	0.65637 (1)	0.24393 (1)	0.06312 (1)	1.465 (5)
Re(2)	0.75017 (1)	0.23360 (1)	−0.00710 (1)	1.492 (5)
P(11)	0.5879 (1)	0.32891 (7)	0.07901 (7)	1.84 (3)
P(12)	0.6959 (1)	0.24831 (7)	0.15876 (7)	1.86 (3)
P(13)	0.5666 (1)	0.17340 (7)	0.08827 (7)	1.93 (3)
P(21)	0.8876 (1)	0.25382 (7)	−0.00427 (7)	1.95 (3)
P(22)	0.7319 (1)	0.28001 (7)	−0.09021 (7)	1.89 (3)
P(23)	0.7693 (1)	0.14642 (7)	−0.05024 (7)	2.02 (3)
C(1)	0.5230 (4)	0.2627 (3)	0.1608 (3)	2.3 (1)
C(2)	0.8675 (4)	0.2112 (3)	−0.1148 (3)	2.4 (1)
C(11)	0.5123 (4)	0.3165 (3)	0.1233 (3)	2.3 (1)
C(12)	0.6068 (4)	0.2564 (3)	0.1944 (3)	2.6 (1)
C(13)	0.4961 (4)	0.2072 (3)	0.1287 (3)	2.6 (1)
C(1M)	0.4623 (4)	0.2715 (3)	0.2005 (3)	3.1 (2)
C(21)	0.9247 (4)	0.2435 (3)	−0.0694 (3)	2.6 (1)
C(22)	0.7936 (4)	0.2476 (3)	−0.1378 (2)	2.4 (1)
C(23)	0.8455 (4)	0.1505 (3)	−0.0961 (3)	2.8 (2)
C(2M)	0.9163 (4)	0.2019 (4)	−0.1614 (3)	3.4 (2)
H(1)	0.721 (3)	0.294 (2)	0.038 (2)	1 (1)*
H(2)	0.743 (3)	0.199 (2)	0.059 (2)	2 (1)*
H(3)	0.637 (3)	0.215 (3)	−0.007 (2)	0 (1)*
Re(3)	0.65592 (2)	0.34607 (1)	0.35836 (1)	3.190 (7)
O(31)	0.5942 (3)	0.3335 (3)	0.2997 (2)	5.4 (2)
O(32)	0.7318 (4)	0.2955 (3)	0.3665 (3)	7.2 (2)
O(33)	0.6972 (4)	0.4126 (3)	0.3564 (3)	7.9 (2)
O(34)	0.6011 (3)	0.3427 (3)	0.4104 (2)	5.2 (1)

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

are available as supplementary material.

Physical Measurements. A Perkin-Elmer 1800 FTIR spectrometer was 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. The $E_{1/2}$ values were determined as $(E_{\text{p,a}} + E_{\text{p,c}})/2$ and referenced to the silver/silver chloride (Ag/AgCl) electrode at room temperature and are uncorrected for junction potentials. Under our experimental conditions the ferrocenium/ferrocene couple is at $E_{1/2} = +0.47$ V vs Ag/AgCl. The ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on a Varian XL-200 spectrometer. Proton resonances were referenced internally to the residual protons in the incompletely deuteriated solvent (δ +7.20 in C_6D_6 and δ +5.30 in CD_2Cl_2). Phosphorus resonances were referenced externally to 85% H_3PO_4.

Table IV. Important Bond Distances (Å) and Bond Angles (deg) for **1**[a]

Bond Distances			
Re–Cl(1)	2.410 (6)	P(2)–C(21)	1.86 (2)
Re–Cl(2)	2.329 (5)	P(3)–C(31)	1.84 (2)
Re–Cl(3)	2.408 (5)	C(10)–C(11)	1.52 (3)
Re–P(1)	2.423 (5)	C(10)–C(14)	1.59 (2)
Re–P(2)	2.509 (5)	C(10)–C(21)	1.60 (3)
Re–P(3)	2.412 (5)	C(10)–C(31)	1.52 (3)
P(1)–C(11)	1.82 (2)		

Bond Angles			
Cl(1)–Re–Cl(2)	86.3 (2)	Cl(2)–Re–P(3)	95.8 (2)
Cl(1)–Re–Cl(3)	86.7 (2)	Cl(3)–Re–P(1)	174.2 (2)
Cl(1)–Re–P(1)	93.2 (2)	Cl(3)–Re–P(2)	89.4 (2)
Cl(1)–Re–P(2)	92.5 (2)	Cl(3)–Re–P(3)	93.9 (2)
Cl(1)–Re–P(3)	177.9 (3)	P(1)–Re–P(2)	84.8 (2)
Cl(2)–Re–Cl(3)	88.3 (2)	P(1)–Re–P(3)	86.1 (2)
Cl(2)–Re–P(1)	97.4 (2)	P(2)–Re–P(3)	85.5 (2)
Cl(2)–Re–P(2)	177.5 (2)		

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

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

Bond Distances			
Re(1)–Re(2)	2.5389 (4)	P(21)–C(21)	1.848 (7)
Re(1)–P(11)	2.335 (2)	P(22)–C(22)	1.847 (7)
Re(1)–P(12)	2.399 (2)	P(23)–C(23)	1.843 (7)
Re(1)–P(13)	2.364 (2)	C(1)–C(11)	1.55 (1)
Re(1)–H(1)	1.76 (5)	C(1)–C(12)	1.538 (9)
Re(1)–H(2)	1.80 (5)	C(1)–C(13)	1.54 (1)
Re(1)–H(3)	1.86 (6)	C(1)–C(1M)	1.54 (1)
Re(2)–P(21)	2.341 (2)	C(2)–C(21)	1.57 (1)
Re(2)–P(22)	2.325 (2)	C(2)–C(22)	1.54 (1)
Re(2)–P(23)	2.328 (2)	C(2)–C(23)	1.54 (1)
Re(2)–H(1)	1.90 (5)	C(2)–C(2M)	1.54 (1)
Re(2)–H(2)	1.86 (5)	Re(3)–O(31)	1.697 (6)
Re(2)–H(3)	1.95 (6)	Re(3)–O(32)	1.715 (7)
P(11)–C(11)	1.826 (7)	Re(3)–O(33)	1.686 (7)
P(12)–C(12)	1.858 (7)	Re(3)–O(34)	1.706 (6)
P(13)–C(13)	1.840 (7)		

Bond Angles			
P(11)–Re(1)–P(12)	82.20 (6)	P(22)–Re(2)–P(23)	89.37 (6)
P(11)–Re(1)–P(13)	100.61 (6)	P(22)–Re(2)–H(1)	101 (2)
P(11)–Re(1)–H(1)	82 (2)	P(22)–Re(2)–H(2)	169 (2)
P(11)–Re(1)–H(2)	156 (2)	P(22)–Re(2)–H(3)	96 (2)
P(11)–Re(1)–H(3)	116 (2)	P(23)–Re(2)–H(1)	167 (2)
P(12)–Re(1)–P(13)	81.67 (6)	P(23)–Re(2)–H(2)	94 (2)
P(12)–Re(1)–H(1)	104 (2)	P(23)–Re(2)–H(3)	91 (2)
P(12)–Re(1)–H(2)	89 (2)	H(1)–Re(2)–H(2)	74 (2)
P(12)–Re(1)–H(3)	161 (2)	H(1)–Re(2)–H(3)	80 (2)
P(13)–Re(1)–H(1)	175 (2)	H(2)–Re(2)–H(3)	73 (2)
P(13)–Re(1)–H(2)	100 (2)	Re(1)–H(1)–Re(2)	88 (2)
P(13)–Re(1)–H(3)	89 (2)	Re(1)–H(2)–Re(2)	88 (2)
H(1)–Re(1)–H(2)	79 (2)	Re(1)–H(3)–Re(2)	84 (2)
H(1)–Re(1)–H(3)	86 (3)	O(31)–Re(3)–O(32)	109.5 (3)
H(2)–Re(1)–H(3)	77 (2)	O(31)–Re(3)–O(33)	109.3 (4)
P(21)–Re(2)–P(22)	86.31 (6)	O(31)–Re(3)–O(34)	109.2 (3)
P(21)–Re(2)–P(23)	89.12 (6)	O(32)–Re(3)–O(33)	108.7 (4)
P(21)–Re(2)–H(1)	100 (2)	O(32)–Re(3)–O(34)	110.5 (3)
P(21)–Re(2)–H(2)	105 (2)	O(33)–Re(3)–O(34)	109.5 (3)
P(21)–Re(2)–H(3)	178 (2)		

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

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

Results

The starting point for the chemistry described in this report is the mononuclear rhenium(III) complex ReCl$_3$(triphos), which was prepared previously by Guntz and Leigh[7] from the complex ReCl$_3$(PPh$_3$)$_2$(NCCH$_3$),[6,10] and ReCl$_3$(PP$_2$), which we obtained

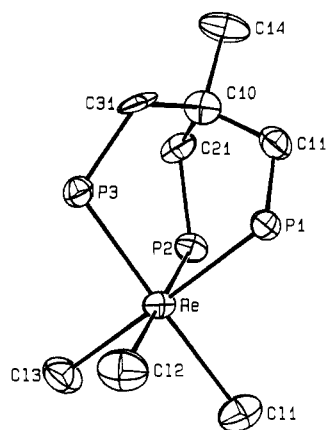(10) Drew, M. G. B.; Tisley, D. G.; Walton, R. A. *Chem. Commun.* **1970**, 600.

Figure 1. ORTEP representation of the structure of $ReCl_3(triphos)$ with the phenyl rings omitted. The thermal ellipsoids are drawn at the 50% probability level.

in a similar fashion from the direct reaction between $ReCl_3-(PPh_3)_2(NCCH_3)$ with PP_2 in hot benzene. Following the completion of our work, Luo and Crabtree[4] described the preparation of $ReCl_3(PP_2)$ from mer-$ReCl_3(PMePh_2)_3$[11] and furthermore used this to prepare $ReH_5(PP_2)$ and, in turn, its protonated derivative $[ReH_6(PP_2)]^+$. We have also obtained both of these polyhydride species, but other than providing details of our preparative procedures in the Experimental Section, we will limit our discussion of them to situations where our data supplements that which has already been published.[4] Overall, our spectroscopic characterizations are in excellent agreement with the results described by Luo and Crabtree.[4]

Few complexes of the type $ReX_3(P_3)$ (where X = halide and P_3 represents a tridentate phosphine) have been prepared previously,[2b] and none have been characterized by X-ray crystallography. Accordingly, we carried out a single-crystal X-ray structure determination on $ReCl_3(triphos)$ at +20 °C. The ORTEP representation of the structure is shown in Figure 1. The important details of the crystallographic and structural parameters are given in Tables I, II, and IV.

The cyclic voltammogram (CV) of $ReCl_3(triphos)$ in 0.1 M $TBAH$-CH_2Cl_2 displays a reversible one-electron process at $E_{1/2}$ = +0.72 V vs Ag/AgCl ($E_{p,a} - E_{p,c}$ = 100 mV and $i_{p,a}/i_{p,c}$ = 1), corresponding to an oxidation of the neutral complex, and two irreversible reductions of $E_{p,c}$ = −0.37 V and $E_{p,c}$ = −0.63 V. The CV of $ReCl_3(PP_2)$ is very similar, with $E_{1/2}(ox)$ = +0.63 V, $E_{p,c}$ = −0.46 V, and $E_{p,c}$ = −0.90 V vs Ag/AgCl.[12]

Interestingly, the compound $ReCl_3(triphos)$ can easily be oxidized to the cationic Re(IV) species $[ReCl_3(triphos)]^+$ by concentrated HNO_3. The resulting red oxidation product can be isolated as the nitrate salt in good yield (88%). Its solutions in acetone (ca. 1 × 10^{-3} M) have conductivities in accord with it being a 1:1 electrolyte (Λ_m = 126 Ω^{-1} cm^2 mol^{-1}). The CV of this salt is analogous to the neutral complex, except that the reversible process at $E_{1/2}$ = +0.72 V corresponds to a reduction of the bulk complex. A similar reaction with nitric acid was attempted with $ReCl_3(PP_2)$, but only decomposition products were observed. The insolubility of the salt $[ReCl_3(triphos)]NO_3$ may aid its stability, while the more soluble derivative containing the PP_2 ligand is apparently oxidized further by nitric acid.

Reactions of $ReCl_3(triphos)$ and $ReCl_3(PP_2)$ with Sodium Borohydride. The reactions of the title complexes with $NaBH_4$ in ethanol produce the yellow complexes $ReH_5(triphos)$ and $Re-H_5(PP_2)$. The latter complex was prepared independently by Luo and Crabtree,[4] whose report appeared following the completion of our own studies. While our NMR spectral measurements on

$ReH_5(PP_2)$ were carried out in a solvent (C_6D_6) different from that used by Luo and Crabtree (CD_2Cl_2),[4] the spectral properties are essentially the same with the exception of the expected solvent shift;[13] the ^1H NMR spectrum shows a triplet of doublets at δ −6.48 ($^2J_{P-H}$ = 14.7 and 9.3 Hz), while the $^{31}P\{^1H\}$ spectrum shows slightly broadened singlets at δ +90.7 and +52.7. These properties accord with a molecule in which the hydride ligands achieve equivalency through fluxionality. The IR spectrum (Nujol mull) with ν(Re–H) at 1952 w, 1918 w, and 1874 w cm^{-1} is in excellent agreement with the literature data.[4]

The complex $ReH_5(triphos)$ had microanalytical data and an IR spectrum which indicate that it contains some water of crystallization. This is not unexpected, given the propensity of rhenium polyhydrides to incorporate lattice solvent molecules, including water.[13-15] A weak broad ν(Re–H) mode is observed at 1956 cm^{-1}. Its ^1H NMR spectrum (recorded in C_6D_6) shows a broad binomial quartet at δ −6.40 ($^2J_{P-H} \approx$ 6 Hz) for the Re–H resonance, while a broad singlet at δ +9.2 is seen in the $^{31}P\{^1H\}$ spectrum.

The compounds $ReH_5(triphos)$ and $ReH_5(PP_2)$ have CV properties (in 0.1 M $TBAH$-CH_2Cl_2 with v = 200 mV s^{-1}) that are characteristic of phosphine complexes of rhenium pentahydride,[16,17] with $E_{p,a}$ = +0.20 V ($E_{p,c}$ = +0.05 V, but $i_{p,a} \gg i_{p,c}$) and $E_{p,a}$ = +0.35 V vs Ag/AgCl, respectively. Both complexes react with $HBF_4 \cdot Et_2O$ in benzene, but only in the case of the PP_2 complex was an identifiable product isolated, namely, $[ReH_6(P-P_2)]BF_4$. Its ^1H NMR spectrum in (CD_2Cl_2) shows a Re–H resonance at δ +5.14 as a triplet of doublets (the literature value is δ +5.11).[4] When the protonation of $ReH_5(triphos)$ is carried out in acetonitrile or propionitrile, the monohydrido complexes $[ReH(NCR)_3(triphos)](BF_4)_2$ are formed (R = Me, Et), a reaction course which resembles that found[18] when $ReH_7(PPh_3)_2$ and $ReH_5(PPh_3)_2L$ (L represents a monodentate ligand) are reacted with $HBF_4 \cdot Et_2O$ in RCN to give $[ReH(NCR)_4(PPh_3)_2]-(BF_4)_2$ and $[ReH(NCR)_3(PPh_3)_2L](BF_4)_2$, respectively. The ^1H NMR spectra of $[ReH(NCR)_3(triphos)](BF_4)_2$ (recorded in CD_2Cl_2) show binomial quartets at δ −6.74 (R = Me) and δ −6.95 (R = Et) with coupling constants ($^2J_{P-H}$ = 36–40 Hz) that are characteristic of seven-coordinate monohydridorhenium(III) complexes.[18,19] The $^{31}P\{^1H\}$ NMR spectra provide further evidence that these species are fluxional since they consist of a singlet at δ −3.4 for R = Me and δ −4.3 for R = Et. The proton-coupled ^{31}P spectra are doublets with $^2J_{P-H} \approx$ 36 Hz, thereby confirming the presence of a single hydride ligand. While the Nujol mull IR spectra of both complexes show intense ν(B–F) modes at 1056–1058 cm^{-1}, the ν(Re–H) and ν(CN) vibrations are exceedingly weak and poorly defined. Their CV's in 0.1 M $TBAH$-CH_2Cl_2 show that these two complexes are much more readily oxidized than the analogous compounds that contain PPh_3,[18] with reversible couples at $E_{1/2}$ = +0.16 V and $E_{1/2}$ = +1.18 V vs Ag/AgCl for R = Me and $E_{1/2}$ = +0.18 V and $E_{1/2}$ = +1.22 V vs Ag/AgCl for R = Et.[20]

Reactions of $ReH_5(triphos)$ with Phosphine, Arsine, and Stibine Ligands. Preliminary experiments showed that $ReH_5(triphos)$ reacts with EPh_3 (E = P, As, Sb) and the bidentate ligands $Ph_2PCH_2CH_2PPh_2$ (dppe) and $Ph_2PCH_2CH_2AsPh_2$ (arphos) to afford trihydrides of composition $ReH_3(triphos)L$, where L =

(11) Luo and Crabtree[4] used the abbreviation triphos for PhP-($CH_2CH_2PPh_2$)$_2$, the same abbreviation used by ourselves and others[5] for $CH_3C(CH_2PPh_2)_3$. To avoid confusion, we use PP_2 as the abbreviation for $PhP(CH_2CH_2PPh_2)_2$ in the present report.

(12) Both $ReCl_3(triphos)$ and $ReCl_3(PP_2)$ are paramagnetic,[4,7] a magnetic moment of 1.8 μ_B having been reported[7] for $ReCl_3(triphos)$.

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(17) Costello, M. T.; Walton, R. A. *Inorg. Chem.* **1988**, *27*, 2563.

(18) Allison, J. D.; Moehring, G. A.; Walton, R. A. *J. Chem. Soc., Dalton Trans.* **1986**, 67.

(19) Leeaphon, M.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1990**, *29*, 4348.

(20) For $[ReH(NCMe)_3(triphos)](BF_4)_2$, the process at $E_{1/2}$ = +1.18 V overlaps one at a slightly more positive potential (by ca. 0.12 V). This could arise from a reversible isomerization that follows the oxidation at ca. +1.2 V. However, we observe no such doubling of the waves in the case of the EtCN derivative.

EPh_3, η^1-dppe, or η^1-arphos. A more efficient and higher yield route to these compounds involves the direct reaction of $ReCl_3$-(triphos) with L and $NaBH_4$ in refluxing ethanol for 1–2 h. These reactions proceed through the intermediacy of ReH_5(triphos), as demonstrated by ^1H NMR spectroscopy. This is the procedure we subsequently used to prepare samples of all these compounds (see Experimental Section). These trihydrides can be protonated by $HBF_4 \cdot Et_2O$ in dichloromethane to give white $[ReH_4(trip$-$hos)L]BF_4$, which are readily deprotonated by NEt_3 to regenerate the parent trihydrides. The spectral and electrochemical properties of these complexes are summarized in Table VI.

The cyclic voltammetric data are very diagnostic of these types of rhenium complexes, with the trihydrides showing a reversible oxidation ($i_{p,a}/i_{p,c} = 1$) with an $E_{1/2}$ value in the range –0.03 to –0.20 V vs Ag/AgCl which is dependent on the nature of L, while for the tetrahydrido cations the most accessible process is an irreversible oxidation with an $E_{p,a}$ value between +1.24 and +1.37 V vs Ag/AgCl (Table VI). These properties are very characteristic of other rhenium trihydrides and tetrahydrido cations that have previously been studied by this technique.[21] In the case of the ReH_3(triphos)L compounds, there are several irreversible oxidation processes at more positive potentials that signal the formation of chemical products following the oxidation to $[ReH_3(triphos)L]^+$. For example, in addition to $E_{1/2}$(ox) at –0.20 V in the CV of $ReCl_3$(triphos)(PPh_3), there are processes at $E_{p,c}$ = +0.22, ca. +0.9, and +1.23 V when a scan rate (v) of 200 mV s^{-1} is used.

The room-temperature ^1H NMR spectra of CD_2Cl_2 or C_6D_6 solutions of these complexes show that the hydride ligands are rendered equivalent by fluxional processes and appear as quartets when L = $AsPh_3$ or $SbPh_3$ and doublets of quartets for the PPh_3 and η^1-dppe derivatives. The $^{31}P\{^1H\}$ spectra of ReH_3(triphos)L, when L = $AsPh_3$ or $SbPh_3$, are singlets, whereas ReH_3(trip-hos)(PPh_3) displays resonances at δ +3.9 (doublet) and δ +45.3 (quartet) in an intensity ratio of 3:1 that can be assigned to the triphos and PPh_3 ligands, respectively. Similar features are found in the $^{31}P\{^1H\}$ NMR spectrum of ReH_3(triphos)(η^1-dppe), where the resonance at δ +4.8 (doublet) is assigned to triphos and that at δ +24.7 (an apparent pentet) is due to the bound phosphorus atom of the η^1-dppe ligand. The uncomplexed P atom of the η^1-dppe ligand is found at δ –11.8 and appears as a doublet due to coupling with the bound P atom.[22] Since both P-P coupling constants are essentially the same, the resonance for the bound P atom of η^1-dppe appears as a pentet.

While the reaction of $ReCl_3$(triphos) with arphos and $NaBH_4$ produces the expected complex ReH_3(triphos)(η^1-arphos), its ^1H and $^{31}P\{^1H\}$ NMR spectra provide clear evidence for the presence of isomers in which the η^1-arphos ligand is either P or As bound. This accords with the results of a previous study[23] in which we isolated the isomers $ReH_5(PPh_3)_2$(arphos-As) and ReH_5-($PPh_3)_2$(arphos-P) from the reaction of $ReH_7(PPh_3)_2$ with arphos. Although we have been unable to separate the mixture of linkage isomers, their spectra are easily distinguishable (see Table VI). There is supporting evidence for the presence of isomers from the CV electrochemical measurements on this product, since the $E_{p,c}$ component of the process at $E_{1/2}$ = –0.14 V consists of two closely spaced components that differ in potential by ca. 50 mV.

The protonated complexes $[ReH_4(triphos)L]BF_4$ possess NMR spectra that in large measure mirror those of the neutral trihydride precursors. The ^1H NMR spectra show Re–H resonances that appear either as doublets of quartets or quartets depending upon whether the ligand L is a phosphorus donor or not. In all cases this resonance appears downfield of that of the corresponding

(21) Moehring, G. A.; Walton, R. A. *J. Chem. Soc., Dalton Trans.* **1987**, 715.

(22) There is plenty of precedent for $^2J_{P-P}$ and $^3J_{P-P}$ coupling constants to be of the magnitude observed in the present case (ca. 34 Hz; see Table VI) for dangling bidentate phosphine ligands of the type $R_2P(CH_2)_nPR_2$ (n = 1, 2). See for example: (a) Woitha, C.; Rehder, D. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1438. (b) Cotton, F. A.; Matusz, M. *Polyhedron* **1987**, *6*, 261.

(23) Costello, M. T.; Fanwick, P. E.; Green, M. A.; Walton, R. A. *Inorg. Chem.* **1991**, *30*, 861.

Table VI. Electrochemical and Spectroscopic Properties of Mononuclear Rhenium Polyhydrides ReH_3(triphos)L and $[ReH_4$(triphos)L]BF_4

	CV half-wave potentials, V[a]				^1H NMR, δ^d			$^{31}P\{^1H\}$ NMR, $\delta^{d,g}$	solvent[h]
complex	$E_{p,a}$	$E_{1/2}$(ox)[b]	ν(Re–H)	ν(Re–H)[c]	Re–H[e]	–CH[f]	–CH$_2$[f]		
ReH_3(triphos)(PPh_3)		–0.20 (80)	1965 vs, 1924 w, 1880 w	–6.77 dq (41.5, 20.0)	+1.22	+2.38	+3.9 d (28.5), +45.3 q (28.5)	C_6D_6
				–7.24 dq (46.5, 18.6)	+1.41	+2.24		CD_2Cl_2
ReH_3(triphos)($AsPh_3$)		–0.14 (85)	1970 m-w, 1884 w	–6.17 q (12.7)	+1.20	+2.39	+5.6 s	C_6D_6
				–6.82 q (12.6)	+1.35	+2.30		CD_2Cl_2
ReH_3(triphos)($SbPh_3$)		–0.03 (100)	1948 m-s, 1882 m-w, 1814 w	–7.04 q (12.7)	+1.22	+2.39	+7.9 s	C_6D_6
				–7.71 q (12.8)	+1.37	+2.32		CD_2Cl_2
ReH_3(triphos)(η^1-dppe)		–0.18 (100)	1994 w, 1954 w	–6.81 dq (29.5, 14.6)	+1.19	+2.30	–11.8 d (35.0), +4.8 d(33.0), +24.7 p (33.5)	C_6D_6
ReH_3(triphos)(arphos-P)		–0.14[i]	j	–6.82 dq (28.0, 14.0)	+1.19	+2.32	+4.9 d (33.0), +25.1 q (33.0)	C_6D_6
ReH_3(triphos)(arphos-As)		–0.14[i]	j	–6.56 q (12.6)	+1.19	+2.32	–12.5 s, +6.5 s	C_6D_6
$[ReH_4$(triphos)(PPh_3)]BF_4	+1.24		≈1990 vw, br	–5.11 dq (31.6, 14.3)	+1.65	+2.53	–3.5 d (24.0), +32.7 q (23.0)	CD_2Cl_2
$[ReH_4$(triphos)($AsPh_3$)]BF_4	+1.32		1968 w, br	–5.25 q (15.1)	+1.69	+2.58	–3.1 s	CD_2Cl_2
$[ReH_4$(triphos)($SbPh_3$)]BF_4	+1.37		2026 vw, 1980 vw, 1948 w	–6.50 q (14.6)	+1.75	+2.64	–2.7 s	CD_2Cl_2
$[ReH_4$(triphos)(η^1-dppe)]BF_4	+1.32		k	–5.44 dq (28.0, 14.0)	+1.68	+2.56	–3.7 d (19.5), +8.6 m, +28.2 m	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 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 those complexes that contain the BF_4^- anion a strong ν(B–F) mode is present at ca. 1060 cm^{-1}. [d] Abbreviations are as follows: s = singlet, d = doublet, dq = doublet of quartets, q = quartet, p = pentet, m = multiplet. [e] $^2J_{P-H}$ coupling constants (in Hz) given in parentheses. [f] CH_3– and –CH_2– resonances of the triphos ligand, which in all instances are singlets. [g] $^2J_{P-P}$ coupling constants (in Hz) given in parentheses. [h] Solvent (C_6D_6 or CD_2Cl_2) used in the ^1H and $^{31}P\{^1H\}$ NMR spectral measurements. [i] The value for this couple is approximate since the $E_{p,c}$ wave consists of two closely spaced components which are probably due to the arphos-P and arphos-As linkage isomers. [j] The mixture of isomers contains weak features at 1994 vw, 1976 w, 1946 w, 1886 w, 1870 vw, 1846 vw, and 1810 vw cm^{-1}. [k] Too weak to be observed.

trihydride. The $^{31}P\{^1H\}$ spectra show patterns similar to those seen in the spectra of the ReH$_3$(triphos)L parents, although in the case of [ReH$_4$(triphos)(η^1-dppe)]BF$_4$ the quality of the spectrum was adversely affected by the poorer solubility properties of this complex.

To examine further the scope of this chemistry, we carried out additional reactions between mixtures of ReCl$_3$(triphos) and various monodentate phosphines with NaBH$_4$ in ethanol with use of the procedure analogous to that described for the preparation of ReH$_3$(triphos)(PPh$_3$). In all instances, yellow products were isolated whose electrochemical and spectral properties were in accord with the stoichiometry ReH$_3$(triphos)(PR$_3$).[24] The CV's of solutions of the PMe$_3$, PEt$_3$, PMe$_2$Ph, PMePh$_2$, and P(OEt)$_3$ complexes in 0.1 M TBAH–CH$_2$Cl$_2$ revealed $E_{1/2}$(ox) values of –0.22, –0.26, –0.23, –0.21, and –0.08 V vs Ag/AgCl, respectively, and their ^1H NMR spectra (in C$_6$D$_6$) showed diagnostic doublet of quartet patterns for the Re–H resonance at δ –6.45, –7.09, –6.37, –6.33, and –7.24, respectively, with $^2J_{P–H}$ values of ca. 24 and ca. 12 Hz. In the case of the products with PEt$_3$, PMePh$_2$, and P(OEt)$_3$, representative $^{31}P\{^1H\}$ NMR spectra were measured and these displayed characteristic doublet and quartet patterns: PEt$_3$, δ +6.8 (d, $^2J_{P–P}$ = 32 Hz) and δ +3.9 (q, $^2J_{P–P}$ = 32 Hz); PMePh$_2$, δ +5.3 (d, $^2J_{P–P}$ = 36 Hz) and δ +0.2 (q, $^2J_{P–P}$ = 36 Hz); P(OEt)$_3$, δ +2.9 (d, $^2J_{P–P}$ = 62 Hz) and δ +139.4 (q, $^2J_{P–P}$ = 62 Hz). Since these properties agree so closely with those found for ReH$_3$(triphos)(PPh$_3$) (Table VI), there can be little doubt that these compounds are structurally very similar.

Conversion of ReH$_5$(triphos) to Re$_2$H$_4$(triphos)$_2$. When the ^1H NMR spectrum of a solution of ReH$_5$(triphos) in C$_6$D$_6$ is monitored over a period of several days at room temperature (+25 °C), the Re–H resonance at δ –6.40 slowly decreases in intensity as the solution acquires a pink coloration and a new resonance appears at δ –7.54. This spectral change signals the conversion of ReH$_5$(triphos) to Re$_2$H$_4$(triphos)$_2$. This reaction proceeds with evolution of H$_2$ (δ +4.65), but with no observable formation of any intermediates (by NMR), and is essentially complete within 8 days. Upon increase of the temperature, the conversion of ReH$_5$(triphos) to Re$_2$H$_4$(triphos)$_2$ becomes very rapid. Thus, the reaction of ReCl$_3$(triphos) with NaBH$_4$ in ethanol gives ReH$_5$-(triphos) in high yield upon heating the reaction mixture for 15 min (see reaction B(i) in the Experimental Section). However, by an increase of the reaction time to ca. 1 h, the product is almost exclusively the dark red dinuclear complex Re$_2$H$_4$(triphos)$_2$ (isolated yield 63%) and there is no evidence for significant quantities of ReH$_5$(triphos) being present.

The complex Re$_2$H$_4$(triphos)$_2$ displays a broad Re–H resonance in its ^1H NMR spectrum at δ –5.74 in C$_6$D$_6$ and δ –5.90 in C$_7$D$_8$; in the latter solvent this spectrum is essentially unchanged over the temperature range +80 to –80 °C. The $^{31}P\{^1H\}$ NMR spectrum consists of a singlet at δ +19.9 in C$_6$D$_6$. The cyclic voltammogram of the complex in 0.1 M TBAH–CH$_2$Cl$_2$ consists of three reversible processes (with $i_{p,a}/i_{p,c}$ = 1 and $\Delta E_p \approx$ 80 mV) at $E_{1/2}$ = +1.17, +0.24, and –0.55 V vs Ag/AgCl, each of which corresponds to a one-electron oxidation of the bulk complex. Solutions of the +2 and +1 cations can be accessed by bulk oxidation, and the integrity of the dinuclear species survives several cycles of such oxidations and reductions. The chemical oxidation of Re$_2$H$_4$(triphos)$_2$ to its green monocation is brought about by several oxidants including oxygen. When a dichloromethane solution of Re$_2$H$_4$(triphos)$_2$ is exposed to air, a clean oxidation ensues. This process was monitored with the use of electronic absorption spectroscopy. The concentration of the red complex, Re$_2$H$_4$(triphos)$_2$ (λ_{max} = 434 nm), decreased over a period of several hours, while that of the green species, [Re$_2$H$_4$(triphos)$_2$]$^+$, which has absorption maxima at 628 and 650 nm, increased. There is an isosbestic point at 548 nm. The oxidation of
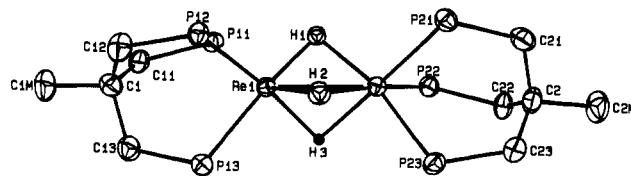

Figure 2. ORTEP representation of the structure of the [Re$_2$H$_4$(triphos)$_2$]$^+$ cation with the phenyl rings omitted. The thermal ellipsoids are drawn at the 50% probability level. One of the hydride ligands was not located but is probably bound to Re(1) (see Discussion).

Re$_2$H$_4$(triphos)$_2$ appears to be first order with no complicating side reactions.

Oxidants such as C$_7$H$_7$PF$_6$ and Ph$_3$CPF$_6$ also effect the oxidation of Re$_2$H$_4$(triphos)$_2$ to [Re$_2$H$_4$(triphos)$_2$]$^+$, but when C$_7$-H$_7$PF$_6$ was used with the objective of preparing [Re$_2$H$_4$(triphos)$_2$]PF$_6$, the perrhenate salt was isolated instead. This reflects not only the presence of adventitious oxygen in the reaction system but also the considerable stability of this particular salt. This same salt was obtained during unsuccessful attempts to obtain single crystals of Re$_2$H$_4$(triphos)$_2$ and of mononuclear ReH$_5$(triphos). Again, small quantities of oxygen must have been present in these systems. It was a crystal from the latter batch that was used in the structure determination of [Re$_2$H$_4$(triphos)$_2$]ReO$_4$. This crystal, which was of composition [Re$_2$H$_4$(triphos)$_2$]ReO$_4$·5C$_6$H$_6$, contained an unusually large number of solvent molecules of crystallization. Nonetheless the structure solved very well with the exception of our failure to locate and refine one of the four hydride ligands that we believe is present. The structure of the dirhenium cation is shown in Figure 2. Details of the crystallographic and structural parameters are provided in Tables I, III, and V. As expected, this complex displayed a poorly defined ^1H NMR spectrum, which consisted of a few broad humps. However, a satisfactory magnetic moment could not be obtained by the Evans method because of the limited solubility of this complex and the very large contribution from the diamagnetic corrections. Also, attempts to obtain an ESR spectrum on a dichloromethane solution of the complex at –160 °C were also unsuccessful for reasons that are unclear.

Discussion

The complex ReH$_5$(triphos) constitutes the second example of a mononuclear rhenium polyhydride with a tripodal phosphine ligand, the first being the complex ReH$_5$(PP$_2$), where PP$_2$ represents PhP(CH$_2$CH$_2$PPh$_2$)$_2$, that was recently described by Luo and Crabtree[4] and prepared independently by ourselves during the course of the present study. The structure of the Re(triphos) unit presumably resembles closely that present in the structurally characterized chloride ReCl$_3$(triphos) (Figure 1), a complex that we used as the synthetic precursor to ReH$_5$(triphos). The structure of ReCl$_3$(triphos) is that of the *fac* isomer, with average Cl–Re–Cl and P–Re–P angles of 87.1 [12] and 85.5 [7]°, respectively. The Re–Cl and Re–P distances, which average 2.382 [53] and 2.448 [61] Å, respectively, are normal for an octahedral Re(III) chloride complex.[10,25] The longest Re–P bond (Re–P(2) = 2.509 (5) Å) is trans to the shortest Re–Cl bond (Re–Cl(2) = 2.329 (5) Å), while the other pairs of Re–Cl and Re–P bond lengths are identical within 3σ.

The variable-temperature ^1H NMR spectra of ReH$_5$(PP$_2$) and [ReH$_6$(PP$_2$)]BF$_4$ have been studied by Luo and Crabtree.[4] While T_1 measurements, as well as studies of the IPR (isotopic perturbation of resonance) effect,[26] have provided evidence[4] that ReH$_5$(PP$_2$) is a classical polyhydride, the [ReH$_6$(PP$_2$)]$^+$ cation may adopt a classical/nonclassical borderline structure. In our study we have not focused our attention on this particular structural question but have instead chosen to explore the reactivity of these pentahydrido complexes in order to ascertain how a

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(24) Isolated yields were generally in excess of 50%. While these products were not subjected to elemental microanalyses, their ^1H NMR spectra integrated in accord with a 1:1 ratio of triphos and PR$_3$ ligands. In the case of the PMe$_3$ reaction, a second product was isolated (^1H NMR: Re–H at δ –7.1 br, s), but its identity remains to be established.

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tripodal tridentate phosphine ligand might influence the reaction chemistry compared to a complex such as $ReH_5(PPh_3)_3$, which contains only monodentate phosphines.

Typically, rhenium complexes of the types $ReH_5(PR_3)_3$ and $ReH_5(PR_3)_2L$ show limited thermal reactivity with nucleophiles, although such compounds can be activated both photochemically[27] and in the presence of electrophiles such as $[C_7H_7]^+$.[21] However, ReH_5(triphos) shows an enhanced thermal reactivity as demonstrated by its reactions with EPh_3 (E = P, As, Sb), dppe, and arphos, which yield the yellow trihydridorhenium complexes ReH_3(triphos)L, where $L = EPh_3$, η^1-dppe, or η^1-arphos. Of particular note is our finding that the η^1-arphos complex exists as a mixture of linkage isomers, ReH_3(triphos)(arphos-*As*) and ReH_3(triphos)(arphos-*P*), a situation which resembles the isolation of linkage isomers of $ReH_5(PPh_3)_2(\eta^1$-arphos).[23] These trihydrides are readily protonated by $HBF_4 \cdot Et_2O$ to give $[ReH_4$(triphos)-L]BF_4, which may in turn be deprotonated by NEt_3. This chemistry resembles that reported for the mixed-ligand conjugate acid–base pairs of the type $[ReH_4(PPh_3)_3L]^+/ReH_3(PPh_3)_3L$, where L = MeCN, *t*-BuNC or xylylNC, which were prepared previously in our laboratory.[21] Note that entry to this latter chemistry is different from that described in the present report since the complexes $[ReH_4(PPh_3)_3L]PF_6$ are obtained[21] by the treatment of $ReH_5(PPh_3)_3$ with $C_7H_7PF_6$ in the presence of the ligand L. Interestingly, not all tetrahydridorhenium cations are as readily deprotonated as $[ReH_4$(triphos)L]$^+$ and $[ReH_4-(PPh_3)_3L]^+$. Thus, Caulton and co-workers[28] found that $[ReH_4(PMe_2Ph)_4]^+$ is not deprotonated by NEt_3, so that in this case the trihydrido complex is a stronger base than NEt_3. Whether this difference reflects the fact that the structures of the triphos- and PPh_3-containing complexes are closer to the nonclassical formulation $[ReH_2(\eta^2-H_2)P_3L]^+$ is unclear.

The comparative ease with which ReH_5(triphos) converts to the trihydrido species ReH_3(triphos)L accords with our observation that, in the absence of any ligand L, the pentahydride ReH_5-(triphos) loses dihydrogen to form the dirhenium polyhydride complex Re_2H_4(triphos)$_2$. This is the first instance where a ReH_5P_3 complex (P represents a tertiary phosphine ligand) has been found to undergo reductive loss of H_2 under *thermal conditions* to afford a dinuclear polyhydride. The complex that is isolated appears to be the neutral dirhenium tetrahydride Re_2H_4(triphos)$_2$.

The dark red complex Re_2H_4(triphos)$_2$ has a very accessible, reversible, one-electron oxidation with an $E_{1/2}$ value of -0.55 V vs Ag/AgCl. Not surprisingly, the green monocationic species is produced very easily from the neutral precursor under a variety of conditions, including aerial oxidation. Indeed it was formed as the majority species during attempts to grow single crystals of both Re_2H_4(triphos)$_2$ and ReH_5(triphos). Benzene solutions of the mononuclear pentahydride slowly evolve H_2 with concomitant dimerization to produce Re_2H_4(triphos)$_2$. In both instances, the presence of small amounts of adventitious oxygen not only results in oxidation of Re_2H_4(triphos)$_2$ to $[Re_2H_4$(triphos)$_2]^+$ but leads to degradation of a portion of the rhenium complex to provide the $[ReO_4]^-$ ion, which stabilizes the $[Re_2H_4$(triphos)$_2]^+$ cation.

The structure of the $[Re_2H_4$(triphos)$_2]^+$ cation as present in the salt $[Re_2H_4$(triphos)$_2]ReO_4 \cdot 5C_6H_6$ is shown in Figure 2. Superficially at least, the structure has the appearance of a face-sharing bioctahedron if we neglect the terminal hydride ligand that was not located in this structure determination. However, there are significant differences between the two halves of the molecule. In particular, the right-hand side of the molecule (as shown in Figure 2) has a more regular geometry, with the trans-P–Re(2)–H angles being in the range 167 (2)–178 (2)°,

while the corresponding angles about Re(1), which range in value from 156 (2) to 175 (2)°, show a greater deviation from linearity. The P–Re(2)–P angles are all close to 90° (86.31 (6)–89.37 (6)°), while the P–Re–P angles about Re(1) are 81.67 (6), 82.20 (6), and 100.61 (6)° and deviate to a much greater extent from 90°. These angular distortions, along with the fact that the Re(1)–P distances are on average longer than the Re(2)–P distances (2.369 versus 2.331 Å) are consistent with a higher coordination number for Re(1) and therefore with the presence of a terminal Re–H bond in the coordination sphere. Since the P(11)–Re(1)–P(13) angle (100.61 (6)°) is the largest of the three, it would be reasonable to locate the missing hydride ligand between P(11) and P(13), i.e. on the backside of the cation as represented in I. The

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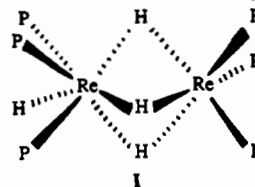
structural parameters for the right-hand side of the complex cation (Figure 2) are very similar to those for the corresponding fragment in the unsymmetrical complex anion $[H_6Re(\mu\text{-}H)_3Re(triphos)]^-$, which has been structurally characterized by Abrahams et al.[5]

The Re–Re bond distance of 2.5389 (4) Å is within the quite narrow range (2.51–2.61 Å) determined[5,14,27b,29–32] for other structurally characterized dirhenium polyhydride complexes that contain phosphines as the only ancillary ligands and possess *three or four* Re–H–Re bridging units. Another compound, $Re_2(\mu\text{-}H)_2H_6(\mu\text{-dppm})_2$, with only two bridging hydrido groups, has a much longer Re–Re bond distance of 2.9335 (9) Å,[15] while the complex cation $[Re_2(\mu\text{-}H)H_4(\mu\text{-dmpm})_3]^+$ with a single bridging hydride, possesses the remarkably long Re–Re distance of 3.5150 (4) Å.[33] This trend reflects the importance of three-center two-electron Re–H–Re bonds in dictating the overall strength of the Re–Re interaction and the Re–Re distance.

In view of the unsymmetrical structure of the $[Re_2H_4$(triphos)$_2]^+$ cation and, by implication, its neutral precursor, the simplicity of the ^1H and $^{31}P\{^1H\}$ NMR spectra of Re_2H_4(triphos)$_2$ (single broad Re–*H* resonance from +80 to −80 °C and a singlet in the $^{31}P\{^1H\}$ spectrum) is in accord with a fluxional process that renders the hydride ligands and phosphorus atoms equivalent in solution on the NMR time scale.

Supplementary Material Available: Tables giving full details of the crystal data and data collection parameters (Tables S1 and S2), positional parameters (Tables S3–S6), anisotropic thermal parameters (Tables S7 and S8), and complete bond distances (Tables S9 and S10) and bond angles (Tables S11 and S12) for **1** and **2** (44 pages); tables of observed and calculated structure factors (54 pages). Ordering information is given on any current masthead page.

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