*Inorg. Chem.* **1987**, *26*, 1861–1866

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# Mixed Polyhydride–Phosphine Clusters That Contain the $Re_2Au$ and $Re_2Au_2$ Cores: Reversible Protonation and Auration of the Dirhenium Polyhydride Complex $Re_2(\mu\text{-}H)_4H_4(PPh_3)_4$

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*Received December 5, 1986*

The dirhenium polyhydride complex $Re_2(\mu\text{-}H)_4H_4(PPh_3)_4$ (**1**) reacts reversibly with $HBF_4{\cdot}Et_2O$ to give $[Re_2H_9(PPh_3)_4]BF_4$ (**2**) and with $[Au(PR_3)]^+$ (R = Ph, Et) to afford the heterometallic clusters $[Re_2H_8(PPh_3)_4Au(PR_3)]PF_6$ (**3a**, R = Ph; **3b**, R = Et) and $[Re_2H_8(PPh_3)_4\{Au(PR_3)\}_2](PF_6)_2$ (**4a**, R = Ph; **4b**, R = Et). The treatment of **2** with $NEt_3$ regenerates **1**, whereas complexes of types **3** and **4** are deprotonated to give $Re_2H_7(PPh_3)_4Au(PR_3)$ (**5a**,**b**) and $[Re_2H_7(PPh_3)_4\{Au(PR_3)\}_2]PF_6$ (**6a**,**b**), respectively. Complexes **5** and **6** can be reprotonated to give **3** and **4**, respectively, while **3** and **4** can in turn be reconverted into **1** by reaction with $Br^-$ or $PPh_3$. The structure of the triangular $Re_2Au$ cluster complex $Re_2H_7(PPh_3)_4Au(PPh_3)$ (**5a**) has been determined by a single-crystal X-ray structure analysis on crystals grown from THF–$CH_3OH$. This complex crystallizes in the monoclinic space group $P2_1/a$ with the following unit cell dimensions: $a = 22.620$ (5) Å, $b = 13.161$ (4) Å, $c = 26.549$ (5) Å, $\beta = 106.94$ (2)°, $V = 7561$ (5) Å$^3$, and $Z = 4$. The structure was refined to $R = 0.045$ ($R_w = 0.059$) for 5915 data with $F^2 > 3.0\sigma(F^2)$. The structure is characterized by a short Re–Re distance (2.571 (1) Å) and inequivalent Re–Au distances (2.927 (1) and 2.720 (1) Å) associated with the bridging $Au(PPh_3)$ group. This distortion may reflect steric congestion that arises from the five $PPh_3$ ligands. The pairs of trans P–Re–P bonds are partially staggered with respect to one another. The seven hydride ligands were not located in this structure analysis. These polyhydride–phosphine complexes, like the parent complex **1**, exhibit a rich redox chemistry as measured by cyclic voltammetry. For example, **5a** and **5b** possess a very accessible one-electron oxidation at $E_{1/2} \simeq -0.4$ V vs. Ag/AgCl. In the case of **5a**, oxidation to paramagnetic $[Re_2H_7(PPh_3)_4Au(PPh_3)]PF_6$ (**7a**) has been accomplished with $(C_7H_7)PF_6$ as the oxidant. The reduction of **7a** back to **5a** occurs with $(\eta^5\text{-}C_5H_5)_2Co$.

## Introduction

Rhenium polyhydride complexes and other transition-metal polyhydrides react with Lewis acids in a variety of ways, including adduct formation, hydride abstraction, and the reductive elimination of $H_2$.[1-7] Following our recent isolation of the salt $[ReH_6(PPh_3)_3]BF_4$ from the reaction of $ReH_5(PPh_3)_3$ with $HBF_4{\cdot}Et_2O$,[1] we have begun to examine the adduct-forming ability of dirhenium polyhydrides, especially the complex $Re_2(\mu\text{-}H)_4H_4(PPh_3)_4$ (**1**).[8] This work has drawn upon our previous studies of the redox chemistry, hydride abstraction reactions, and substitution chemistry of **1** and other complexes of this type.[3,9] In the present report we describe the protonation reactions of **1** and its reactions with the isolobal[10-13] species $[Au(PR_3)]^+$ (R = Ph, Et) to give mixed Re–Au clusters.

## Experimental Section

**Starting Materials.** The complex $Re_2(\mu\text{-}H)_4H_4(PPh_3)_4$ was prepared by the standard literature method.[8] Most other reagents and solvents were obtained from commercial sources. Solvents were deoxygenated and/or distilled prior to use. All reactions were carried out under an atmosphere of nitrogen.

**A. Protonation of $Re_2(\mu\text{-}H)_4H_4(PPh_3)_4$ (1). $[Re_2H_9(PPh_3)_4]BF_4$ (2).** A suspension of **1** (0.103 g, 0.069 mmol) in 5 mL of $CH_2Cl_2$ was treated with $HBF_4{\cdot}Et_2O$ (0.10 mL, 0.15 mmol). The mixture was stirred for 10 min, and diethyl ether (30 mL) and *n*-pentane (4 mL) were then added. The resulting rust-colored crystals of $[Re_2H_9(PPh_3)_4]BF_4{\cdot}{}^3/_4CH_2Cl_2$ were filtered off, washed three times with diethyl ether, and then dried under vacuum; yield 0.095 g (91%). Anal. Calcd for $C_{72.75}H_{70.5}BCl_{1.5}F_4P_4Re_2$: C, 55.26; H, 4.49. Found: C, 55.19; H, 4.68. The amount of $CH_2Cl_2$ of crystallization was confirmed by $^1$H NMR spectroscopy ($\delta = +5.35$ in acetone-$d_6$).

**B. Reactions of $Re_2(\mu\text{-}H)_4H_4(PPh_3)_4$ (1) with $[Au(PR_3)]^+$ (R = Ph, Et). (i) $[Re_2H_8(PPh_3)_4Au(PPh_3)]PF_6$ (3a).** A solution of $[Au(PPh_3)]PF_6$ was prepared by stirring $AuCl(PPh_3)$ (0.033 g, 0.067 mmol) and $AgPF_6$ (0.017 g, 0.067 mmol) in 5 mL of acetone for 5 min and filtering to remove the insoluble AgCl.[14] This solution was then mixed with a stoichiometric quantity of **1** (0.100 g, 0.066 mmol) in 5 mL of $CH_2Cl_2$, whereupon the red suspension quickly turned dark green. This mixture was stirred for 10 min, 30 mL of diethyl ether was added, and the mixture was stirred for an additional 5 min. It was then filtered into 75 mL of *n*-pentane and the resulting yellow-green precipitate filtered off, washed with diethyl ether, and dried under vacuum; yield 0.107 g (79%). Anal. Calcd for $C_{90}H_{83}AuF_6P_6Re_2$: C, 53.15; H, 4.11. Found: C, 52.72; H, 4.34.

**(ii) $[Re_2H_8(PPh_3)_4\{Au(PPh_3)\}_2](PF_6)_2$ (4a).** An acetone solution (5 mL) of $[Au(PPh_3)]PF_6$ (0.14 mmol), prepared as described in paragraph B(i), was mixed with **1** (0.102 g, 0.068 mmol) in 5 mL of $CH_2Cl_2$. The mixture was stirred for 10 min and then filtered into 100 mL of diethyl ether. The resulting green-brown precipitate was filtered off and dried under vacuum; yield 0.052 g (30%). Anal. Calcd for $C_{108}H_{98}Au_2F_{12}P_8Re_2$: C, 49.17; H, 3.74. Found: C, 49.04; H, 3.88.

When the filtrate from this reaction was mixed with 100 mL of *n*-pentane, a yellow-green precipitate of **3a** formed. This was filtered off and dried under vacuum; yield 0.078 g (56%). This product was identified on the basis of its spectroscopic and electrochemical properties.

The complex **4a** was also formed upon reacting a $CH_2Cl_2$ solution (5 mL) of **3a** (0.117 g, 0.058 mmol) with 1 equiv of $[Au(PPh_3)]PF_6$ (0.059 mmol) in 5 mL of acetone. Workup led to **4a** together with some unreacted **3a**; yield 0.044 g (63%).

**(iii) $[Re_2H_8(PPh_3)_4Au(PEt_3)]PF_6$ (3b).** A solution containing $[Au(PEt_3)]PF_6$ (0.14 mmol), prepared by reacting $AuCl(PEt_3)$ (0.049 g, 0.14 mmol) with $AgPF_6$ (0.035 g, 0.14 mmol) in 5 mL of acetone, was reacted with a suspension of **1** (0.100 g, 0.066 mmol) in 5 mL of $CH_2Cl_2$. The mixture was stirred for 10 min and then filtered into 50 mL of diethyl ether. The resulting green-brown precipitate was filtered off and set aside (see paragraph B(iv)), while the filtrate was mixed with 50 mL of *n*-pentane to give a yellow-green solid; yield 0.033 g (26%). Anal. Calcd

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[14] This procedure works equally well when $TlPF_6$ is used in place of $AgPF_6$ and/or with $AuBr(PPh_3)$ in place of $AuCl(PPh_3)$.

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for $C_{78}H_{83}AuF_6P_6Re_2$: C, 49.31; H, 4.40; P, 9.78. Found: C, 49.35; H, 4.70; P, 9.60.

**(iv) $[Re_2H_8(PPh_3)_4\{Au(PEt_3)\}_2](PF_6)_2$ (4b).** The initial insoluble green-brown reaction product that was isolated in the preceding reaction (paragraph B(iii)) was dried under vacuum; yield 0.098 g (63%). Anal. Calcd for $C_{84}H_{98}Au_2F_{12}P_8Re_2$: C, 42.93; H, 4.20. Found: C, 42.70; H, 3.92.

This complex was also obtained in 44% yield upon reacting **3b** with 1 equiv of $[Au(PEt_3)]PF_6$ in $CH_2Cl_2$–acetone solution by a procedure like that described in paragraph B(ii).

**C. Deprotonation Reactions. (i) Conversion of 2 to 1.** An acetone solution (5 mL) of **2** (0.090 g, 0.057 mmol) was treated with 0.5 mL of triethylamine and the mixture stirred for ca. 3 min. The red precipitate of **1** was filtered off and dried under vacuum; yield 0.078 g (96%). This product was identified on the basis of a comparison of its properties to those of authentic samples.[3,8]

**(ii) Conversion of 3a to $Re_2H_7(PPh_3)_4Au(PPh_3)$ (5a).** A mixed methanol (10 mL)–ethanol (5 mL) solution of **3a** (0.089 g, 0.044 mmol) was treated with 0.5 mL of $Et_3N$. This mixture was stirred for 30 min and the red precipitate of **5a** filtered off and dried under vacuum; yield 0.072 g (89%). Anal. Calcd for $C_{90}H_{82}AuP_5Re_2$: C, 57.26; H, 4.38. Found: C, 56.77; H, 4.75.

**(iii) Conversion of 3b to $Re_2H_7(PPh_3)_4Au(PEt_3)$ (5b).** A procedure similar to that in paragraph C(ii) gave **5b**, yield 31%. Anal. Calcd for $C_{78}H_{82}AuP_5Re_2$: C, 53.72; H, 4.74. Found: C, 54.64; H, 4.21.

**(iv) Conversion of 4a to $[Re_2H_7(PPh_3)_4\{Au(PPh_3)\}_2]PF_6$ (6a).** A quantity of **4a** (0.053 g, 0.020 mmol) in methanol (10 mL)–acetone (5 mL) was treated with 1.0 mL of $Et_3N$. The mixture was stirred for 30 min and 8 mL of $H_2O$ then added. The red precipitate was filtered off, washed with diethyl ether followed by *n*-pentane, and dried under vacuum; yield 0.040 g (80%). Anal. Calcd for $C_{108}H_{97}Au_2F_6P_7Re_2$: C, 52.05; H, 3.92. Found: C, 50.87; H, 3.91.

**(v) Conversion of 4b to $[Re_2H_7(PPh_3)_4\{Au(PEt_3)\}_2]PF_6$ (6b).** A procedure similar to that in paragraph C(iv) gave **6b**, yield 67%. Anal. Calcd for $C_{84}H_{97}Au_2F_6P_7Re_2$: C, 45.78; H, 4.44. Found: C, 46.08; H, 4.53.

**D. Reactions of $Re_2H_7(PPh_3)_4Au(PR_3)$ (5a, R = Ph; 5b, R = Et). (i) Reaction of 5a with $[Au(PPh_3)]PF_6$.** Equimolar quantities of **5a** (0.061 g, 0.032 mmol) dissolved in $CH_2Cl_2$ (5 mL) and $[Au(PPh_3)]PF_6$ (0.033 mmol) in acetone (5 mL) were mixed, and the mixture was stirred for 10 min and then filtered into a mixture of diethyl ether (50 mL) and *n*-pentane (50 mL). The resulting red precipitate was filtered off and dried under vacuum; yield 0.056 g (70%). The product was identified as $[Re_2H_7(PPh_3)_4\{Au(PPh_3)\}_2]PF_6$ (**6a**) on the basis of its electrochemical and spectroscopic properties.

**(ii) Reaction of 5b with $[Au(PEt_3)]PF_6$.** The complex **5b** was converted into $[Re_2H_7(PPh_3)_4\{Au(PEt_3)\}_2]PF_6$ (**6b**) by using a procedure similar to that described in paragraph D(i); yield 46%. The product was identified on the basis of its spectroscopic and electrochemical properties.

**(iii) Protonation of 5a.** A solution of **5a** (0.048 g, 0.025 mmol) in 5 mL of $CH_2Cl_2$ was acidified with $HBF_4{\cdot}Et_2O$ (0.10 mL, 0.15 mmol), the mixture was stirred for 5 min, and diethyl ether (50 mL) and *n*-pentane (50 mL) were added. The green complex $[Re_2H_8(PPh_3)_4Au(PPh_3)]BF_4$ precipitated and was filtered off and dried under vacuum; yield 0.027 g (54%). Its identity was based upon a comparison of the spectroscopic and electrochemical properties of this complex with those of a sample of **3a**.

**(iv) Protonation of 5b.** The complex $Re_2H_7(PPh_3)_4Au(PEt_3)$ (**5b**) was protonated by $HBF_4{\cdot}Et_2O$ to give $[Re_2H_8(PPh_3)_4Au(PEt_3)]BF_4$ by a procedure analogous to that given in paragraph D(iii); yield 33%.

**E. Deauration Reactions. (i) Reaction of $[Re_2H_8(PPh_3)_4Au(PPh_3)]PF_6$ (3a) with Bromide.** An acetone solution (5 mL) of **3a** (0.093 g, 0.046 mmol) was treated with $n\text{-}Bu_4NBr$ (0.045 g, 0.14 mmol) and the mixture stirred for 10 min. The red precipitate of **1** was filtered off and dried under vacuum; yield 0.062 g (91%). This product was identified through a comparison of its spectroscopic and electrochemical properties with literature data.[3,8]

**(ii) Reaction of $[Re_2H_8(PPh_3)_4Au(PEt_3)]PF_6$ (3b) with Triphenylphosphine.** A reaction similar to that given in paragraph E(i) occurred upon reacting **3b** with an excess of $PPh_3$ in acetone to afford **1**; yield 75%.

**(iii) Reaction of $[Re_2H_8(PPh_3)_4\{Au(PPh_3)\}_2](PF_6)_2$ (4a) with Triphenylphosphine.** The reaction between **4a** and $PPh_3$ in acetone afforded **1** in high yield; yield 89%.

**(iv) Reaction of $[Re_2H_8(PPh_3)_4\{Au(PEt_3)\}_2](PF_6)_2$ (4b) with Bromide.** A procedure analogous to that given in paragraph E(i) converted **4b** into **1**; yield 90%.

**F. Redox Chemistry of $Re_2H_7(PPh_3)_4Au(PPh_3)$ (5a). (i) Oxidation to $[Re_2H_7(PPh_3)_4Au(PPh_3)]PF_6$ (7a).** A quantity of $Re_2H_7(PPh_3)_4Au(PPh_3)$ (0.041 g, 0.022 mmol) was suspended in 5 mL of $CH_2Cl_2$ and treated with $(C_7H_7)PF_6$ (0.007 g, 0.03 mmol). The red suspension changed to a dark green. After a reaction time of 10 min the solution was filtered into 100 mL of a 1:1 mixture of diethyl ether and *n*-pentane and the resulting blue-green solid filtered off and dried under vacuum. Anal. Calcd for $C_{90}H_{82}AuF_6P_6Re_2$: C, 53.17; H, 4.07. Found: C, 51.47; H, 4.24.

**Table I.** Crystallographic Data and Data Collection Parameters for $Re_2H_7(PPh_3)_4Au(PPh_3)$[a]

| | |
|---|---|
| formula | $AuRe_2P_5C_{90}H_{82}$ |
| fw | 1887.89 |
| space group | $P2_1/a$ |
| $a$, Å | 22.620 (5) |
| $b$, Å | 13.161 (4) |
| $c$, Å | 26.549 (5) |
| $\beta$, deg | 106.94 (2) |
| $V$, Å$^3$ | 7561 (5) |
| $Z$ | 4 |
| $d_{calcd}$, g cm$^{-3}$ | 1.658 |
| cryst dimens, mm | 0.35 × 0.24 × 0.19 |
| temp, °C | 22.0 |
| radiation (wavelength, Å) | Mo K$\alpha$ (0.71073) |
| monochromator | graphite |
| linear abs coeff, cm$^{-1}$ | 53.19 |
| abs cor applied | empirical[b] |
| diffractometer | Enraf-Nonius CAD4 |
| scan method | $\theta$–$2\theta$ |
| *hkl* limits | −22 to 22, 0 to 10, 0 to 28 |
| $2\theta$ range, deg | 4.00–45.00 |
| scan width, deg | $0.80 + 0.35 \tan \theta$ |
| takeoff angle, deg | 4.90 |
| programs used | Enraf-Nonius SDP |
| $F_{000}$ | 3704.0 |
| $p$ factor used in weighting | 0.070 |
| unique data | 10354 |
| data with $I > 3.0\sigma(I)$ | 5919 |
| no. of variables | 433 |
| largest shift/esd in final cycle | 0.08 |
| $R$[c] | 0.045 |
| $R_w$[d] | 0.059 |
| goodness of fit[e] | 1.114 |

[a] Numbers in parentheses following certain data are estimated standard deviations occurring in the least significant digits. [b] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 158. [c] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F_o)$. [e] Goodness of fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

**(ii) Reduction of 7a to 5a.** A stoichiometric mixture of **7a** (0.075 g, 0.037 mmol) and $(\eta^5\text{-}C_5H_5)_2Co$ (0.014 g, 0.042 mmol) in acetone (5 mL) was stirred for 5 min and then treated with 10 mL of methanol. The precipitated **5a** was filtered off and dried under vacuum; yield 0.038 g (55%). The identity of this product was confirmed by its spectroscopic and electrochemical properties.

**Preparation of Single Crystals of $Re_2H_7(PPh_3)_4Au(PPh_3)$ (5a).** A single crystal of **5a** was obtained by dissolving a sample of **5a** in 0.5 mL of THF and layering 1.5 mL of MeOH over this solution in a small test tube. Good quality crystals were allowed to grow for 3 days before they were harvested.

**X-ray Structure Determination.** A large crystal with dimensions 0.35 × 0.24 × 0.19 mm was mounted on a glass fiber with epoxy cement. The crystal was indexed, and data were collected on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator and a standard-focus molybdenum X-ray tube. Crystal data and information relating to data collection and structure refinement are listed in Table I. The cell parameters are based on 25 reflections with $12.85 < \theta < 18.55°$. Three standard reflections were measured after every 1 h of beam exposure during data collection and displayed no systematic variation in intensity. Further details of the crystal data collection and reduction methods we used are available elsewhere.[15]

Calculations were performed on a PDP 11/34 computer using the Enraf-Nonius structure determination package. The structure was refined in the nonstandard monoclinic space group $P2_1/a$ (standard space group $P2_1/c$, No. 14). An empirical absorption correction was applied.[16] The linear absorption coefficient was 53.19 cm$^{-1}$. No correction for extinction was applied. The least-squares program minimized the

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

| atom | *x* | *y* | *z* | *B*, Å$^2$ |
|---|---|---|---|---|
| Au | 0.22152 (3) | 0.05717 (4) | 0.25700 (3) | 2.98 (1) |
| Re(1) | 0.26789 (3) | 0.26328 (4) | 0.28536 (2) | 2.09 (1) |
| Re(2) | 0.20033 (3) | 0.22097 (4) | 0.19172 (2) | 2.14 (1) |
| P | 0.2217 (2) | −0.1001 (3) | 0.2931 (2) | 3.2 (1) |
| P(11) | 0.3735 (2) | 0.2949 (3) | 0.3076 (2) | 2.59 (9) |
| P(12) | 0.2494 (2) | 0.2827 (3) | 0.3671 (2) | 2.62 (9) |
| P(21) | 0.1210 (2) | 0.3331 (3) | 0.1455 (2) | 2.68 (9) |
| P(22) | 0.2081 (2) | 0.0968 (3) | 0.1290 (2) | 2.81 (9) |
| C(11) | 0.2548 (7) | −0.199 (1) | 0.2630 (6) | 3.6 (3)* |
| C(12) | 0.3008 (9) | −0.174 (2) | 0.2393 (8) | 5.6 (5)* |
| C(13) | 0.3270 (9) | −0.255 (2) | 0.2154 (8) | 6.0 (5)* |
| C(14) | 0.307 (1) | −0.350 (2) | 0.2150 (9) | 7.4 (6)* |
| C(15) | 0.264 (1) | −0.379 (2) | 0.2405 (9) | 6.8 (5)* |
| C(16) | 0.2352 (8) | −0.302 (1) | 0.2643 (7) | 4.5 (4)* |
| C(21) | 0.2659 (7) | −0.109 (1) | 0.3620 (6) | 2.9 (3)* |
| C(22) | 0.3229 (8) | −0.163 (1) | 0.3771 (7) | 4.2 (4)* |
| C(23) | 0.3572 (8) | −0.166 (1) | 0.4308 (7) | 5.0 (4)* |
| C(24) | 0.3340 (8) | −0.117 (1) | 0.4683 (7) | 4.7 (4)* |
| C(25) | 0.2780 (8) | −0.062 (1) | 0.4532 (7) | 4.9 (4)* |
| C(26) | 0.2458 (8) | −0.059 (1) | 0.3999 (7) | 4.1 (4)* |
| C(31) | 0.1432 (7) | −0.139 (1) | 0.2906 (6) | 3.1 (3)* |
| C(32) | 0.0966 (8) | −0.106 (1) | 0.2476 (7) | 4.5 (4)* |
| C(33) | 0.0344 (9) | −0.132 (1) | 0.2450 (7) | 5.1 (4)* |
| C(34) | 0.0224 (8) | −0.190 (2) | 0.2863 (8) | 5.3 (4)* |
| C(35) | 0.0694 (9) | −0.219 (2) | 0.3271 (8) | 5.6 (5)* |
| C(36) | 0.1307 (8) | −0.196 (1) | 0.3308 (7) | 5.0 (4)* |
| C(1111) | 0.4037 (6) | 0.330 (1) | 0.2515 (5) | 2.2 (3)* |
| C(1112) | 0.4658 (7) | 0.324 (1) | 0.2563 (6) | 3.5 (3)* |
| C(1113) | 0.4895 (8) | 0.365 (1) | 0.2170 (7) | 4.0 (4)* |
| C(1114) | 0.4499 (8) | 0.406 (1) | 0.1713 (7) | 4.3 (4)* |
| C(1115) | 0.3872 (8) | 0.413 (1) | 0.1671 (7) | 4.4 (4)* |
| C(1116) | 0.3631 (8) | 0.372 (1) | 0.2068 (7) | 4.5 (4)* |
| C(1121) | 0.4067 (6) | 0.403 (1) | 0.3515 (5) | 2.6 (3)* |
| C(1122) | 0.4069 (7) | 0.501 (1) | 0.3310 (6) | 3.4 (3)* |
| C(1123) | 0.4249 (8) | 0.586 (1) | 0.3647 (7) | 4.3 (4)* |
| C(1124) | 0.4416 (8) | 0.573 (1) | 0.4193 (7) | 4.7 (4)* |
| C(1125) | 0.4386 (8) | 0.476 (1) | 0.4397 (7) | 4.6 (4)* |
| C(1126) | 0.4226 (7) | 0.390 (1) | 0.4070 (6) | 2.9 (3)* |
| C(1131) | 0.4266 (7) | 0.191 (1) | 0.3369 (6) | 2.9 (3)* |
| C(1132) | 0.4061 (7) | 0.093 (1) | 0.3221 (6) | 3.9 (4)* |
| C(1133) | 0.4416 (9) | 0.005 (2) | 0.3435 (8) | 5.5 (5)* |
| C(1134) | 0.4975 (9) | 0.023 (2) | 0.3850 (8) | 5.9 (5)* |
| C(1135) | 0.5189 (9) | 0.119 (2) | 0.4006 (8) | 5.6 (5)* |
| C(1136) | 0.4845 (8) | 0.206 (1) | 0.3739 (7) | 4.2 (4)* |
| C(1211) | 0.3131 (7) | 0.254 (1) | 0.4290 (6) | 2.8 (3)* |
| C(1212) | 0.3479 (7) | 0.166 (1) | 0.4301 (6) | 3.0 (3)* |
| C(1213) | 0.3978 (7) | 0.145 (1) | 0.4750 (6) | 3.7 (4)* |
| C(1214) | 0.4124 (8) | 0.211 (1) | 0.5167 (7) | 4.4 (4)* |
| C(1215) | 0.3775 (8) | 0.298 (1) | 0.5169 (7) | 4.1 (4)* |
| C(1216) | 0.3269 (7) | 0.321 (1) | 0.4717 (6) | 3.5 (3)* |
| C(1221) | 0.2283 (7) | 0.411 (1) | 0.3844 (6) | 2.8 (3)* |
| C(1222) | 0.1750 (7) | 0.430 (1) | 0.3995 (6) | 3.6 (3)* |
| C(1223) | 0.1635 (8) | 0.529 (1) | 0.4147 (7) | 4.2 (4)* |
| C(1224) | 0.2054 (8) | 0.604 (1) | 0.4190 (7) | 4.7 (4)* |
| C(1225) | 0.2584 (8) | 0.584 (1) | 0.4029 (7) | 4.3 (4)* |
| C(1226) | 0.2698 (7) | 0.491 (1) | 0.3842 (6) | 3.9 (4)* |
| C(1231) | 0.1881 (7) | 0.202 (1) | 0.3816 (6) | 3.1 (3)* |
| C(1232) | 0.1435 (7) | 0.158 (1) | 0.3407 (6) | 3.0 (3)* |
| C(1233) | 0.0969 (7) | 0.093 (1) | 0.3512 (6) | 3.5 (3)* |
| C(1234) | 0.0990 (8) | 0.077 (1) | 0.4043 (7) | 4.1 (4)* |
| C(1235) | 0.1432 (8) | 0.121 (1) | 0.4450 (7) | 4.9 (4)* |
| C(1236) | 0.1900 (7) | 0.186 (1) | 0.4336 (6) | 3.3 (3)* |
| C(2111) | 0.1381 (7) | 0.427 (1) | 0.0991 (6) | 3.2 (3)* |
| C(2112) | 0.0913 (9) | 0.467 (2) | 0.0586 (8) | 5.3 (4)* |
| C(2113) | 0.107 (1) | 0.542 (2) | 0.0266 (9) | 6.7 (5)* |
| C(2114) | 0.1665 (9) | 0.570 (2) | 0.0345 (8) | 6.2 (5)* |
| C(2115) | 0.2138 (9) | 0.532 (2) | 0.0741 (8) | 5.6 (5)* |
| C(2116) | 0.1971 (8) | 0.458 (1) | 0.1072 (7) | 4.7 (4)* |
| C(2121) | 0.0442 (7) | 0.286 (1) | 0.1041 (6) | 3.6 (3)* |
| C(2122) | −0.0099 (7) | 0.311 (1) | 0.1143 (6) | 3.8 (4)* |
| C(2123) | −0.0672 (9) | 0.275 (2) | 0.0811 (8) | 5.4 (4)* |
| C(2124) | −0.0674 (9) | 0.210 (2) | 0.0409 (8) | 5.7 (5)* |
| C(2125) | −0.014 (1) | 0.188 (2) | 0.0288 (8) | 6.4 (5)* |
| C(2126) | 0.044 (1) | 0.224 (2) | 0.0623 (8) | 6.2 (5)* |
| C(2131) | 0.0970 (6) | 0.419 (1) | 0.1917 (6) | 2.8 (3)* |
| C(2132) | 0.0978 (8) | 0.527 (1) | 0.1844 (7) | 4.3 (4)* |
| C(2133) | 0.0782 (9) | 0.583 (2) | 0.2229 (7) | 5.2 (4)* |
| C(2134) | 0.0602 (9) | 0.537 (2) | 0.2624 (7) | 5.3 (4)* |
| C(2135) | 0.0603 (8) | 0.433 (1) | 0.2678 (7) | 4.4 (4)* |
| C(2136) | 0.0797 (7) | 0.374 (1) | 0.2324 (6) | 3.3 (3)* |
| C(2211) | 0.1871 (7) | 0.131 (1) | 0.0579 (6) | 3.6 (3)* |
| C(2212) | 0.2164 (7) | 0.217 (1) | 0.0476 (6) | 3.9 (4)* |
| C(2213) | 0.2041 (9) | 0.249 (2) | −0.0091 (8) | 6.0 (5)* |
| C(2214) | 0.161 (1) | 0.186 (2) | −0.0488 (9) | 6.5 (5)* |
| C(2215) | 0.1338 (9) | 0.105 (2) | −0.0354 (8) | 6.1 (5)* |
| C(2216) | 0.1473 (8) | 0.072 (1) | 0.0186 (7) | 4.6 (4)* |
| C(2221) | 0.2872 (7) | 0.048 (1) | 0.1350 (6) | 3.1 (3)* |
| C(2222) | 0.2981 (8) | 0.000 (1) | 0.0909 (7) | 4.6 (4)* |
| C(2223) | 0.3594 (9) | −0.042 (2) | 0.0982 (8) | 5.5 (5)* |
| C(2224) | 0.4052 (8) | −0.028 (1) | 0.1421 (7) | 4.9 (4)* |
| C(2225) | 0.3955 (9) | 0.024 (2) | 0.1836 (8) | 5.9 (5)* |
| C(2226) | 0.3348 (8) | 0.065 (1) | 0.1780 (7) | 4.8 (4)* |
| C(2231) | 0.1626 (7) | −0.022 (1) | 0.1234 (6) | 3.4 (3)* |
| C(2232) | 0.0996 (8) | −0.013 (1) | 0.1162 (7) | 4.4 (4)* |
| C(2233) | 0.0627 (9) | −0.098 (2) | 0.1110 (8) | 5.4 (5)* |
| C(2234) | 0.0873 (9) | −0.195 (2) | 0.1126 (8) | 5.7 (5)* |
| C(2235) | 0.1502 (9) | −0.205 (2) | 0.1202 (8) | 6.0 (5)* |
| C(2236) | 0.1898 (8) | −0.118 (1) | 0.1264 (7) | 4.1 (4)* |

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. Starred values are for atoms refined isotropically.

**Table III.** Important Bond Distances (Å) for $Re_2H_7(PPh_3)_4Au(PPh_3)$[a]

| | | | | | |
|---|---|---|---|---|---|
| Au–Re(1) | 2.9266 (8) | P–C(11) | 1.81 (2) | P(12)–C(1231) | 1.88 (2) |
| Au–Re(2) | 2.7197 (8) | P–C(21) | 1.81 (1) | P(21)–C(2111) | 1.86 (2) |
| Au–P | 2.281 (4) | P–C(31) | 1.83 (2) | P(21)–C(2121) | 1.87 (1) |
| Re(1)–Re(2) | 2.5713 (8) | P(11)–C(1111) | 1.87 (2) | P(21)–C(2131) | 1.86 (2) |
| Re(1)–P(11) | 2.325 (4) | P(11)–C(1121) | 1.85 (1) | P(22)–C(2211) | 1.86 (2) |
| Re(1)–P(12) | 2.339 (5) | P(11)–C(1131) | 1.84 (1) | P(22)–C(2221) | 1.86 (2) |
| Re(2)–P(21) | 2.371 (4) | P(12)–C(1211) | 1.88 (1) | P(22)–C(2231) | 1.85 (2) |
| Re(2)–P(22) | 2.376 (4) | P(12)–C(1221) | 1.85 (2) | | |

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

function $w(|F_o| - |F_c|)^2$, where the weighting factor $w = 1/\sigma^2(F_o)$. Only the Re, Au, and P atoms were refined anisotropically, and corrections for anomalous scattering were applied to these atoms.[17] Hydrogen atoms were not included in the final least-squares refinement. The final residuals were $R = 0.045$ and $R_w = 0.059$, and the final difference Fourier map displayed no peaks of chemical significance.

Several attempts were made to locate and refine the seven hydride ligands associated with the dirhenium unit. While several reasonable hydride positions were obtained from difference Fourier maps, in all cases refinement was unsatisfactory. Either the Re–H distance became unreasonably short (<1.5 Å) or the temperature factors became either negative or greater than 20. A second method for obtaining hydrogen positions was to calculate positions by using the neutron diffraction structure data of Bau et al.[18] for $Re_2(\mu\text{-}H)_4H_4(PEt_2Ph)_4$ as a guide to

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(17) (a) Cromer, D. T. In *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.

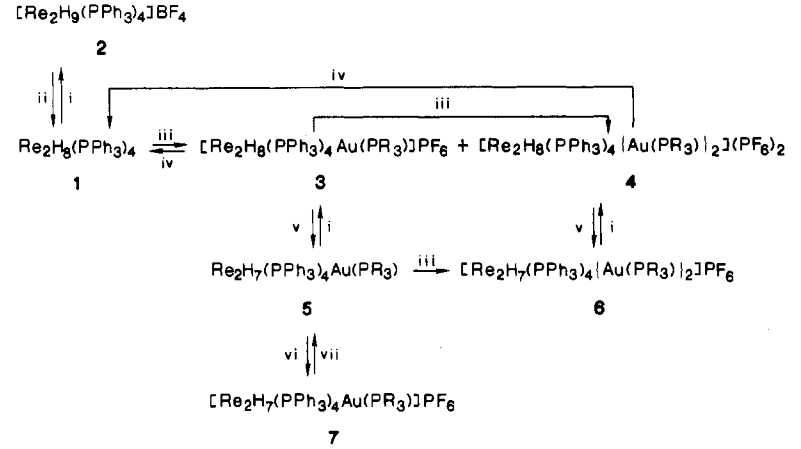
(18) Bau, R.; Carroll, W. E.; Teller, R. G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 3872.

**Table IV.** Important Bond Angles (deg) for $Re_2H_7(PPh_3)_4Au(PPh_3)$[a]

| | | | | | |
|---|---|---|---|---|---|
| Re(1)-Au-Re(2) | 54.03 (2) | Au-P-C(11) | 114.9 (6) | C(1211)-P(12)-C(1221) | 98.6 (6) |
| Re(1)-Au-P | 140.9 (1) | Au-P-C(21) | 114.4 (5) | C(1211)-P(12)-C(1231) | 97.5 (7) |
| Re(2)-Au-P | 164.9 (1) | Au-P-C(31) | 111.0 (5) | C(1221)-P(12)-C(1231) | 101.9 (7) |
| Au-Re(1)-Re(2) | 58.87 (2) | C(11)-P-C(21) | 102.9 (7) | Re(2)-P(21)-C(2111) | 118.9 (5) |
| Au-Re(1)-P(11) | 119.7 (1) | C(11)-P-C(31) | 107.6 (7) | Re(2)-P(21)-C(2121) | 122.1 (5) |
| Au-Re(1)-P(12) | 101.1 (1) | C(21)-P-C(31) | 105.3 (7) | Re(2)-P(21)-C(2131) | 111.1 (4) |
| Re(2)-Re(1)-P(11) | 124.2 (1) | Re(1)-P(11)-C(1111) | 115.4 (4) | C(2111)-P(21)-C(2121) | 99.6 (7) |
| Re(2)-Re(1)-P(12) | 134.73 (9) | Re(1)-P(11)-C(1121) | 119.7 (5) | C(2111)-P(21)-C(2131) | 100.9 (7) |
| P(11)-Re(1)-P(12) | 101.1 (1) | Re(1)-P(11)-C(1131) | 118.1 (5) | C(2121)-P(21)-C(2131) | 100.9 (7) |
| Au-Re(2)-Re(1) | 67.10 (2) | C(1111)-P(11)-C(1121) | 97.9 (7) | Re(2)-P(22)-C(2211) | 119.6 (6) |
| Au-Re(2)-P(21) | 142.1 (1) | C(1111)-P(11)-C(1131) | 100.0 (7) | Re(2)-P(22)-C(2221) | 116.2 (5) |
| Au-Re(2)-P(22) | 82.3 (1) | C(1121)-P(11)-C(1131) | 102.0 (6) | Re(2)-P(22)-C(2231) | 118.9 (6) |
| Re(1)-Re(2)-P(21) | 120.8 (1) | Re(1)-P(12)-C(1211) | 119.5 (6) | C(2211)-P(22)-C(2221) | 97.2 (7) |
| Re(1)-Re(2)-P(22) | 133.02 (9) | Re(1)-P(12)-C(1221) | 117.4 (5) | C(2211)-P(22)-C(2231) | 98.7 (7) |
| P(21)-Re(2)-P(22) | 105.3 (1) | Re(1)-P(12)-C(1231) | 118.1 (5) | C(2221)-P(22)-C(2231) | 102.4 (7) |

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

**Scheme I**[a]



[a] R = (a) Ph or (b) Et. Legend for arrows: (i) $HBF_4{\cdot}Et_2O$ in $CH_2Cl_2$; (ii) $Et_3N$ in acetone; (iii) $[Au(PR_3)]PF_6$ in $CH_2Cl_2$–acetone; (iv) $n$-$Bu_4NBr$ in acetone; (v) $Et_3N$ in MeOH, EtOH, or acetone; (vi) $(C_7H_7)PF_6$ in $CH_2Cl_2$; (vii) $(\eta^5\text{-}C_5H_5)_2Co$ in acetone.

Re–H distances and angles. The refinement again was unsatisfactory. Refining individual, several, or all seven hydrogens leads to the same result. The highest peak in the final difference Fourier was 1.366 e Å$^3$ and is near both rheniums. Consequently, it appears that there is no way to obtain reliable hydrogen positions from the current data set.

Further details concerning the data set, the structure solution, and the structure refinement may be obtained from P.E.F. Table II lists the atomic positional parameters and their errors while Tables III and IV list important intramolecular bond distances and angles. Tables listing thermal parameters (Table S1) and listings of bond distances and bond angles for the phenyl ring carbon atoms (Tables S2 and S3, respectively) are available as supplementary material, as well as a figure (Figure S1) that shows the full atomic numbering scheme.

**Physical Measurements.** Infrared spectra were recorded as Nujol mulls between KBr plates with an IBM Instruments IR 32 Fourier transform (4800–400 cm$^{-1}$) spectrometer. Magnetic susceptibility measurements on dichloromethane solutions of the complexes were measured by the Evans method[19] with the use of a Perkin-Elmer R32 NMR spectrometer. Electrochemical measurements were carried out on dichloromethane solutions that contained 0.1 M tetra-$n$-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the silver/silver chloride (Ag/AgCl) electrode at room temperature and are uncorrected for junction potentials.[20] Voltammetric experiments were performed with a Bioanalytical Systems, Inc., Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035B x-y recorder. $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-200 spectrometer operated at 80.98 MHz using an internal deuterium lock and 85% $H_3PO_4$ as an external standard. Positive chemical shifts were measured downfield from $H_3PO_4$. $^1H$ NMR spectra were obtained on a Varian XL-200 spectrometer. Resonances were referenced internally to the residual protons of $CD_2Cl_2$. Conductivities were measured on an Industrial Instruments Inc. Model RC 16B2 conductivity bridge.

**Analytical Procedures.** Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University microanalytical laboratory.

## Results and Discussion

**A. The Polyhydride Cation $[Re_2H_9(PPh_3)_4]^+$.** Upon treatment of the dirhenium polyhydride complex $Re_2(\mu\text{-}H)_4H_4(PPh_3)_4$ (**1**) with $HBF_4{\cdot}Et_2O$ in the noncoordinating solvent $CH_2Cl_2$, the monoprotonation product $[Re_2H_9(PPh_3)_4]BF_4$ (**2**) is isolated in high yield (>90%; see Scheme I). This reaction is analogous to the protonation of mononuclear $ReH_5(PPh_3)_3$ under similar conditions to give $[ReH_6(PPh_3)_3]BF_4$.[1] The $^1H$ NMR spectrum of **2** (recorded in $CD_2Cl_2$) consists of a multiplet at ca. $\delta$ +7.4 due to the phenyl protons and a pentet at $\delta$ −4.1 ($J$(P–H) = 9.5 Hz) arising from the hydride ligands, while the $^{31}P\{^1H\}$ NMR spectrum consists of a single resonance ($\delta$ +34.6 referenced to $H_3PO_4$). In the event that complex **2** contains a coordinated dihydrogen ligand,[21] a reasonable structural representation of this complex would be as $[Re_2(\mu\text{-}H)_4H_3(PPh_3)_4(L)]BF_4$, where L = $H_2$. This is a likely formulation since analogous species are known in the case of L = MeCN, EtCN, PhCN, and $t$-BuNC.[3] An alternative structural formulation for **2** is as $[Re_2(\mu\text{-}H)_5H_4(PPh_3)_4]BF_4$, an interesting possibility that is raised by the work of Hoffmann and co-workers.[22] Unfortunately, we are not yet able to differentiate between these possibilities since on the NMR time scale all nine hydride ligands are rendered equivalent, as are the four phosphine ligands, by a fluxional process that is not frozen

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(19) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

(20) Electrochemical measurements were carried out by using the experimental procedure described elsewhere; see: Zietlow, T. C.; Klendworth, D. D.; Nimry, T.; Salmon, D. J.; Walton, R. A. *Inorg. Chem.* **1981**, *20*, 947. Under these same experimental conditions the ferrocenium/ferrocene couple has $E_{1/2}$ = +0.47 V vs. Ag/AgCl.

(21) See, for example: Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032.

(22) Dedieu, A.; Albright, T. A.; Hoffmann, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 3141.

**Table V.** Cyclic Voltammetric Data for Mixed Rhenium–Gold Polyhydride Complexes[a]

| complex | $E_{p,a}$ | $E_{1/2}(ox)^b$ | $E_{p,c}$ |
|---|---|---|---|
| $[Re_2H_8(PPh_3)_4Au(PPh_3)]PF_6$ (**3a**) | ~+1.15 | +0.45 (130) | −1.65 |
| $[Re_2H_8(PPh_3)_4Au(PEt_3)]PF_6$ (**3b**) | ~+1.3 | +0.53 (180) | ~−1.7 |
| $Re_2H_7(PPh_3)_4Au(PPh_3)^c$ (**5a**) | +0.30 | −0.45 (100) | |
| $Re_2H_7(PPh_3)_4Au(PEt_3)^c$ (**5b**) | +0.30 | −0.40 (100) | |
| $[Re_2H_7(PPh_3)_4Au(PPh_3)]PF_6^c$ (**7a**) | +0.30 | $-0.45^d$ | |

[a] Measured on 0.1 M TBAH–$CH_2Cl_2$ solutions by the cyclic voltammetric technique (in V vs. Ag/AgCl); scan rate 200 mV/s. [b] For this process $i_{p,a}/i_{p,c} \simeq 1$. Values of $E_{p,a} - E_{p,c}$ (in mV) are given in parentheses. [c] These complexes display an additional irreversible oxidation at $E_{p,a} \simeq +0.9$ V. [d] $E_{1/2}$(red) value.

out even at −80 °C. The cyclic voltammogram (CV) of **2** in 0.1 M TBAH–$CH_2Cl_2$ (Pt-bead electrode) shows well-defined but irreversible redox processes at $E_{p,a} = +1.05$ V and $E_{p,c} = -1.25$ V (at $v = 200$ mV $s^{-1}$) vs. Ag/AgCl; this is quite different from the related behavior of the parent complex **1**,[3] thereby signaling a significant structural difference. Nonetheless, the close relationship of **1** and **2** is demonstrated by the near-quantitative reconversion of **2** to **1** upon its reaction with triethylamine in acetone (see Scheme I).[23]

**B. Auration Reactions of $Re_2(\mu\text{-}H)_4H_4(PPh_3)_4$.** In view of the isolobal relationship[10–13] between $H^+$ and $[Au(PR_3)]^+$, we had anticipated that **1** would react with such gold(I) cations. This expectation has been realized. When $Re_2(\mu\text{-}H)_4H_4(PPh_3)_4$ (**1**) was treated with 1 equiv of a solution of $[Au(PPh_3)]PF_6$ in $CH_2Cl_2$–acetone, the yellow-brown monogold adduct $[Re_2H_8(PPh_3)_4Au(PPh_3)]PF_6$ (**3a**) was isolated in ca. 80% yield. With 2 equiv of $[Au(PPh_3)]PF_6$ a separable mixture of this same monogold complex **3a** and the yellow-brown digold adduct $[Re_2H_8(PPh_3)_4\{Au(PPh_3)\}_2](PF_6)_2$ (**4a**) was formed in which these components were isolable in yields of 30% and 56%, respectively (Scheme I). Similar procedures can be used to prepare the related complexes that are derived from $[Au(PEt_3)]^+$ (**3b** and **4b**). As expected, the treatment of **3a** and **3b** with 1 equiv of the appropriate $[Au(PR_3)]PF_6$ reagent affords **4a** and **4b**, respectively, in good yield.

Among the noteworthy reactions that **3** and **4** undergo is their reconversion to the starting complex **1** upon treatment with the bases $Br^-$ and $PPh_3$ (see Scheme I). These deauration reactions of the heterometallic clusters, which are analogous to the deprotonation of **2** by $NEt_3$ to yield **1**, proceed cleanly in yields of at least 75%. Interestingly, the treatment of **3** and **4** with $NEt_3$ in methanol, ethanol, or acetone (or various mixtures of these solvents) gave the deprotonation products $Re_2H_7(PPh_3)_4Au(PR_3)$ (**5a**, R = Ph; **5b**, R = Et) and $[Re_2H_7(PPh_3)_4\{Au(PR_3)\}_2]PF_6$ (**6a**, R = Ph; **6b**, R = Et), respectively (see Scheme I). Since we completed this work, we have learned that Pignolet and coworkers[24] have independently prepared **6a**. Of special note is the finding that the FABMS technique can be used[24] to confirm the number of hydride ligands.

In view of the redox chemistry displayed by $Re_2(\mu\text{-}H)_4H_4(PPh_3)_4$ and other complexes of this kind,[3] specifically the accessibility of a reversible one-electron oxidation, we expected that these mixed Re–Au clusters would likewise display a quite rich redox chemistry. Each pair of complexes of types **3**–**6** (see Scheme I) exhibits very similar electrochemical properties in 0.1 M TBAH–$CH_2Cl_2$ as measured by the CV technique (Pt-bead electrode).[20] However, these properties are in turn quite different from one pair to another. For example, in the case of $Re_2H_7(PPh_3)_4Au(PPh_3)$ (**5a**) we find $E_{p,a} = +0.95$ V, $E_{p,a} = +0.30$ V, and $E_{1/2} = -0.45$ V, whereas $[Re_2H_7(PPh_3)_4\{Au(PPh_3)\}_2]PF_6$ (**6a**) has $E_{p,a} \simeq +1.10$ V, $E_{1/2} = +0.15$ V, and $E_{p,c} = -1.90$ V vs. Ag/AgCl. Their $Au(PEt_3)$ analogoues **5b** and **6b** have electrochemical properties very similar to these. Electrochemical data for the $Re_2Au$ cluster complexes are summarized in Table V.[25] Since we began these investigations we have been informed by Professor L. H. Pignolet that he is conducting studies of the redox behavior of the $Re_2Au_2$ clusters (**4** and **6**). Therefore, we have not examined their redox characteristics in the same detail that we have those of **3** and **5** and, consequently, a discussion of these results is deferred until a later data.[26] In the case of **5a**, we found that it can be oxidized chemically by using $(C_7H_7)PF_6$ in $CH_2Cl_2$ to form the dark blue-green one-electron-oxidized species $[Re_2H_7(PPh_3)_4Au(PPh_3)]PF_6$ (**7a**).[27] A solution of this complex in $CH_2Cl_2$ has a magnetic moment of ca. 2.0 $\mu_B$ (as measured by the Evans method).[19] The reduction of this complex to re-form **5a** was easily accomplished by using an acetone solution of $(\eta^5\text{-}C_5H_5)_2Co$ as the reducing agent.

**C. Structural Considerations.** In the case of the $Re_2Au$ complexes **3** and **5**, the derivatives with R = Ph showed the greatest stability in solution and the most structurally informative NMR spectra. The pertinent data are summarized in Table VI. For **3a**, the $^1H$ NMR spectrum (in $CD_2Cl_2$) showed a pentet of doublets at $\delta$ −3.41 for Re–*H* with resolvable coupling to the phosphines bound to the dirhenium unit (*J*(P–H) = 10.1 Hz) and the phosphine bound to the gold atom (*J*(P–H) = 3.1 Hz). Its $^{31}P\{^1H\}$ NMR spectrum (in $CD_2Cl_2$) displayed singlets at $\delta$ +71.3 (Au–*P*) and $\delta$ +32.8 (Re–*P*) showing the correct integration. The spectra of the (triethylphosphine)gold analogue **3b** were similar to those of **3a** (Table VI) although the instability of this complex in solution led to the growth of peaks due to impurities. Complex **5a** exhibited analogous spectral features, with $\delta$ ca. −5.6 (broad multiplet, Re–*H*) in its $^1H$ NMR spectrum and $\delta$ +73.0 (broad singlet, Au–*P*) and $\delta$ +42.9 (broad singlet, Re–*P*) in the $^{31}P\{^1H\}$ NMR spectrum. We were unable to obtain NMR spectra of complex **5b** that were of sufficient quality to report the details here. The spectra of **3a** and **5a** revealed little temperature dependence down to −90 °C, which clearly reflects the fluxional nature of these species.

The related $^1H$ and $^{31}P\{^1H\}$ NMR spectral data for the $Re_2Au_2$ cluster complexes **4a**, **4b**, **6a**, and **6b** are also listed in Table VI. In the case of **6b**, two sets of hydride resonances ($\delta$ −3.05 and −5.56) as well as a more complex $^{31}P\{^1H\}$ NMR spectrum may well signal the presence of two isomers. This possibility is given credence by the recent work of Caulton et al.,[28] who have succeeded in isolating and characterizing two isomers of the neutral complex $Re_2H_6(PMe_2Ph)_4\{Au(PPh_3)\}_2$ that were obtained by the reaction of $Re_2H_8(PMe_2Ph)_4$ with 2 equiv of *t*-$BuOAuPPh_3$. One of these isomers contains two bridging $Au(PPh_3)$ groups, while the other probably possesses one bridging and one terminally bound $Au(PPh_3)$ group. If this is the situation with **6b**, we tentatively assign the phosphorus resonances at $\delta$ +69.5 (Au–*P*) and $\delta$ +33.7 (Re–*P*) to one isomer and those at $\delta$ +70.5 and +69.0 (both Au–*P*) and $\delta$ +33.0 (Re–*P*) to the less symmetrical one. Further examination of the possibility of structural isomerism in these $Re_2Au_2$ clusters is under way.[26]

A single-crystal X-ray structure analysis on a crystal of **5a** that was grown from THF–$CH_3OH$ has confirmed the presence of a metal–metal-bonded $Re_2Au$ cluster. Although we have been unable to locate the seven hydride ligands, the triangular nature of the $Re_2Au$ cluster is clearly established (Figure 1). The short

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(23) Other properties of **2** are as follows. The conductivity of a solution in acetone (ca. 1 × $10^{-3}$ M) corresponds to that of a 1:1 electrolyte ($\Lambda$ = 120 $\Omega^{-1}$ $cm^2$ $mol^{-1}$). While several weak bands are seen in the $\nu$(Re–H) region of the IR spectrum of **2** (recorded as a Nujol mull), the most prominent of which is at 1984 m-w $cm^{-1}$, these spectral features are not of any great diagnostic value.

(24) Boyle, P. D.; Johnson, B. J.; Alexander, B. D.; Casalnuovo, J. A.; Gannon, P. R.; Johnson, S. M.; Larka, E. A.; Mueting, A. M.; Pignolet, L. H. submitted for publication in *Inorg. Chem.*

(25) Conductance data on acetonitrile solutions (ca. 1 × $10^{-3}$ M) of **3**, **4**, **6**, and **7** are in accord with their formulation (Scheme I) as 1:1 or 1:2 electrolytes; $\Lambda$ values are ca. 120 $\Omega^{-1}$ $cm^2$ $mol^{-1}$ (for **3**, **6**, and **7**) and 240 $\Omega^{-1}$ $cm^2$ $mol^{-1}$ (for **4**), respectively.

(26) Pignolet, L. H.; et al., unpublished results.

(27) The complex $[Re_2H_7(PPh_3)_4\{Au(PEt_3)\}_2]PF_6$ (**6b**) was oxidized to purple $[Re_2H_7(PPh_3)_4\{Au(PEt_3)\}_2](PF_6)_2$ (yield 67%) by using $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ in acetone.

(28) Caulton, K. G.; Sutherland, B. L.; Folting, K. *Abstracts of Papers*, 192nd National Meeting of the American Chemical Society, Anaheim, CA; American Chemical Society: Washington, DC, 1986; INOR 71. Caulton, K. G., private communication.

**Table VI.** Summary of NMR Spectral Data for Mixed Rhenium–Gold Polyhydride Complexes[a]

| complex | $^1$H NMR, $\delta$[b]<br>Re–*H* | $^{31}$P{$^1$H} NMR, $\delta$[c]<br>Au–*P* | <br>Re–*P* |
|---|---|---|---|
| $[Re_2H_8(PPh_3)_4Au(PPh_3)]PF_6$ (**3a**) | −3.41 (p of d; *J*(P–H) = 10.1, 3.1) | +71.3 (1) | +32.8 (4) |
| $[Re_2H_8(PPh_3)_4Au(PEt_3)]PF_6$ (**3b**) | −3.43 (p of d; *J*(P–H) = 10.2, 3.0)[d] | +72.1 (1)[e] | +32.9 (4)[e] |
| $[Re_2H_8(PPh_3)_4\{Au(PPh_3)\}_2](PF_6)_2$ (**4a**) | −2.75 (m)[e] | +66.8 (1)[e] | +25.7 (2)[e] |
| $[Re_2H_8(PPh_3)_4\{Au(PEt_3)\}_2](PF_6)_2$ (**4b**) | −2.86 (p of t; *J*(P–H) = 11.1, 5.7) | +68.1 (1) | +27.7 (2) |
| $Re_2H_7(PPh_3)_4Au(PPh_3)$ (**5a**) | ~−5.6 (m)[f] | +73.0 (1) | +42.9 (4) |
| $[Re_2H_7(PPh_3)_4\{Au(PPh_3)\}_2]PF_6$ (**6a**) | −3.04 (p of t; *J*(P–H) = 9.0, 4.9) | +70.9 (1) | +33.5 (2) |
| $[Re_2H_7(PPh_3)_4\{Au(PEt_3)\}_2]PF_6$ (**6b**) | −3.05 (m)[g] | +69.5 (1)[g] | +33.7 (2)[g] |

[a] Spectra recorded in $CD_2Cl_2$. Abbreviations are as follows: m = multiplet, p of d = pentet of doublets, *p* of t = pentet of triplets. [b] Coupling constants, *J*(P–H), given in parentheses in Hz, are for coupling to Re–*P* and Au–*P*, respectively. [c] All resonances are singlets. Numbers in parentheses are relative intensities. [d] Related spectrum in $(CD_3)_2CO$ shows $\delta$ −3.63 (p of d; *J*(P–H) = 9.8, 2.9). [e] Spectrum shows presence of impurities. [f] Very broad, poorly resolved resonance. [g] Additional resonances, perhaps due to a different structural isomer, are as follows: $^1$H NMR, $\delta$ −5.56 (m); $^{31}$P{$^1$H} NMR, $\delta$ +70.5 and +69.0 (Au–*P*) and $\delta$ +33.0 (Re–*H*).

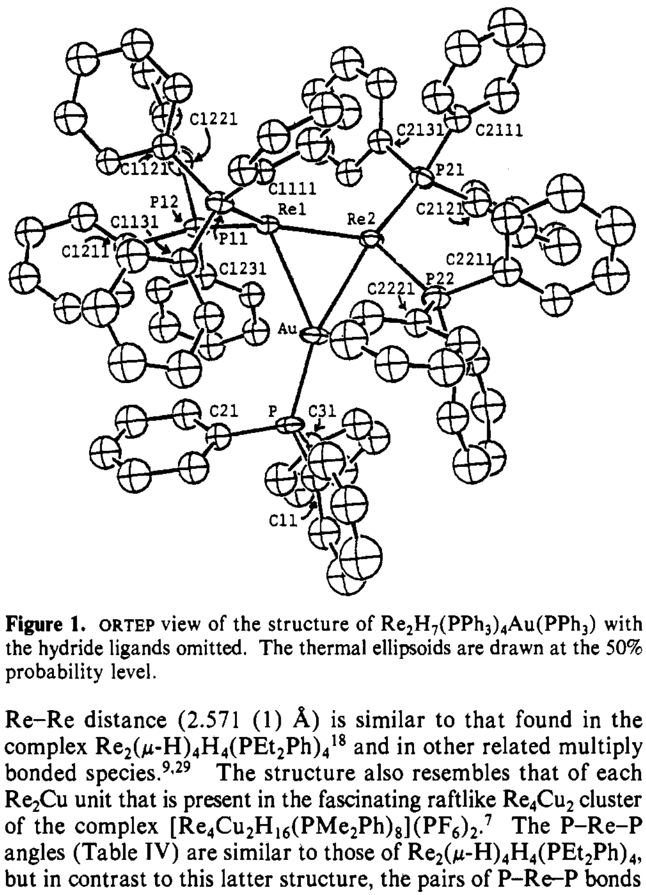
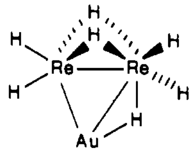


**Figure 1.** ORTEP view of the structure of $Re_2H_7(PPh_3)_4Au(PPh_3)$ with the hydride ligands omitted. The thermal ellipsoids are drawn at the 50% probability level.

Re–Re distance (2.571 (1) Å) is similar to that found in the complex $Re_2(\mu\text{-}H)_4H_4(PEt_2Ph)_4$[18] and in other related multiply bonded species.[9,29] The structure also resembles that of each $Re_2Cu$ unit that is present in the fascinating raftlike $Re_4Cu_2$ cluster of the complex $[Re_4Cu_2H_{16}(PMe_2Ph)_8](PF_6)_2$.[7] The P–Re–P angles (Table IV) are similar to those of $Re_2(\mu\text{-}H)_4H_4(PEt_2Ph)_4$, but in contrast to this latter structure, the pairs of P–Re–P bonds are partially staggered with respect to one another (the angle between the $ReP_2$ planes is 60.6 [1]°). This structural feature resembles that seen within the pairs of $Re_2P_4$ units of $[Re_4Cu_2H_{16}(PMe_2Ph)_8](PF_6)_2$.[7] On the basis of these structural considerations it seems likely that there are two terminal Re–H bonds on each Re atom, each pair being in a partially staggered rotational geometry with respect to the other, and three bridging hydride ligands. In the case of the previously characterized Re–Au clusters $[Au_5ReH_4(PPh_3)_7]^{2+}$[5] and $[Re_3(\mu\text{-}H)_3(CO)_9Au(PPh_3)]^-$,[30] the Au atoms bridge at least three other metal atoms. In the smaller cluster **5a** a doubly bridging mode is encountered, as is the case for one of the isomers of $Re_2H_6(PMe_2Ph)_4\{Au(PPh_3)\}_2$.[28] Of interest is the distortion of the triangular cluster such that the Re(2)–Au distance is shorter than Re(1)–Au by ca. 0.2 Å (see Table III). This distortion leads to a fairly short Au···P(22) contact of ~3.36 Å (Figure 1). This may reflect steric congestion in the crystalline state that arises from the $PPh_3$ ligands or, perhaps more likely, an unsymmetrical disposition of the three bridging hydride ligands about the $Re_2Au$ unit:[31]



**D. Concluding Remarks.** The reversible formation of mixed Re–Au clusters as summarized in Scheme I expands considerably the scope of the chemistry that has been reported previously for the mixed-metal clusters that are formed upon reacting the *mononuclear* rhenium polyhydride complexes $ReH_7(PR_3)_2$ ($PR_3$ = $PPh_3$, P-*i*-$Pr_2Ph$)[5,6] and $ReH_5(PR_3)_3$ ($PR_3$ = $PMePh_2$, $PMe_2Ph$)[7] with the coinage metals. An interesting aspect of the chemistry of $Re_2(\mu\text{-}H)_4H_4(PPh_3)_4$ (**1**) and $Re_2H_7(PPh_3)_4Au(PPh_3)$ (**5a**) is that they are, to our knowledge, the first examples of polyhydride complexes that undergo *both* reversible oxidation and reversible protonation. Furthermore, from the present work the three complexes $[Re_2H_9(PPh_3)_4]BF_4$, $[Re_2H_8(PPh_3)_4Au(PR_3)]PF_6$, and $[Re_2H_7(PPh_3)_4\{Au(PR_3)\}_2]PF_6$ constitute an isoelectronic series within which $H^+$ is substituted by the isolobal $[Au(PR_3)]^+$. As this process occurs, the $Re_2$ core becomes demonstrably more electron-rich as measured by cyclic voltammetry; i.e., the most accessible oxidation decreases in this same order (viz. $E_{p,a}$ = +1.05, ≃+0.5, and ≃+0.2 V, respectively).

Studies directed toward the synthesis and structural characterization of small Re–Au clusters, specifically those derived from the trinuclear $Re_2Au$ core, are continuing.

**Acknowledgment.** We thank the National Science Foundation (Grant No. CHE85-06702) for support of this work and the National Institutes of Health (Grant No. RR-01077 from the Division of Research Resources) for funds for the purchase of the Varian XL-200 spectrometer. We are grateful to Professors L. H. Pignolet and K. G. Caulton for helpful discussions concerning their own studies on these and related systems.[24,26,28] In particular we thank Professor Pignolet for a copy of ref 24 prior to its publication.

**Supplementary Material Available:** Listings of anisotropic thermal parameters (Table S1), bond distances for the phenyl rings (Table S2), and bond angles for the phenyl rings (Table S3) and a figure showing the full atomic numbering scheme (Figure S1) (6 pages); a listing of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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(30) Beringhelli, T.; Ciani, G.; D'Alfonso, G.; DeMaldè, V.; Freni, M. *J. Chem. Soc., Chem. Commun.* **1986**, 735.

(31) We thank Professor K. G. Caulton for suggesting this possibility.