4424 *Inorg. Chem.* **1988**, *27*, 4424-4429

Contribution from the Department of Chemistry,
University of Minnesota, Minneapolis, Minnesota 55455

Redox and Acid-Base Chemistry of $[Au_2Re_2(H)_6(PPh_3)_6]PF_6$ and Related Cluster Compounds

Paul D. Boyle, David C. Boyd, Ann M. Mueting, and Louis H. Pignolet*

Received June 13, 1988

The redox behavior of $[Au_2Re_2(H)_6(PPh_3)_6]PF_6$ (**1**(PF_6)) has been investigated by both cyclic voltammetry and chemical redox reactions. The role of the nitrate ion in the synthesis of **1** from $Re_2(H)_8(PPh_3)_4$ and $Au(PPh_3)NO_3$ has also been investigated, and NO_3^- has been found to cause the oxidation of the intermediate $[Au_2Re_2(H)_8(PPh_3)_6]^{2+}$ (**4**). This has been confirmed by the reaction of **4**$(BF_4)_2$, prepared by an alternate route, with $(PPN)NO_3$ to yield **1**(BF_4). Complex **1** exhibits two quasi-reversible waves in the cyclic voltammogram, an oxidation of $E_{1/2} = 67$ mV (versus Ag/AgCl) giving rise to $[Au_2Re_2(H)_6(PPh_3)_6]^{2+}$ (**2**) and a reduction at $E_{1/2} = -713$ mV to yield $Au_2Re_2(H)_6(PPh_3)_6$ (**3**). Spectroelectrochemical experiments on the oxidation show the clean conversion of **1** to **2**. Complex **2** may be prepared by reaction of **1** with ferrocenium, and **3** may be prepared by reaction of **1** with either sodium naphthalenide or potassium *tert*-butoxide. Complex **2** may be reduced back to **1** by reaction with H_2, and **3** may be oxidized back to **1** by reaction with $(PPN)NO_3$ (PPN = (μ-nitrido)bis(triphenylphosphorus)(1+)) in the presence of $HBF_4{\cdot}Et_2O$. Compound **3** also reacts with $HBF_4{\cdot}Et_2O$ to yield **4**. $Re_2(H)_8(PPh_3)_4$ has been found to react with $[(Ph_3PAu)_3O]BF_4$ to give $[Au_2Re_2(H)_7(PPh_3)_6]BF_4$ (**5**(BF_4)) in good yield. This compound has been found to undergo a quasi-reversible oxidation by cyclic voltammetry, $E_{1/2} = 148$ mV. Spectroelectrochemical studies of the oxidation show the clean conversion to the oxidized species, $[Au_2Re_2(H)_7(PPh_3)_6]^{2+}$. This species may be prepared by the reaction of **5** with ferrocenium and may be rereduced by the reaction with H_2.

Introduction

In a number of recent papers the synthesis and characterization of mixed-metal cluster compounds containing gold have been reported.[1-27] The general synthetic routes to these compounds have included the reaction of carbonyl metalates with $AuPR_3X$ (X = halide or weakly coordinating anion),[25] the replacement of metal hydride ligands by $AuPR_3^+$ units,[8] and the formation of new clusters by the reduction of $AuPR_3^+$ moieties in the presence of a coordinately unsaturated transition-metal compound.[6] Only a few reports, however, have appeared on the addition of $AuPR_3^+$ to multiply bonded metal-metal bonds as a way of building mixed-metal cluster compounds containing gold. We have previously reported the synthesis of $[Au_2Re_2(H)_6(PPh_3)_6]PF_6$ using this method.[4] Recent reports by Caulton et al.[26] and Walton et al.[27] have also shown the efficacy of this method for the preparation of mixed-metal cluster compounds. Our studies on the paramagnetic cluster cation $[Au_2Re_2(H)_6(PPh_3)_6]^+$ (**1**) showed this compound to have a rich acid-base and redox chemistry. We have also found that the nitrate counterion of the gold(I) phosphine precursor has a marked effect on the course of the reaction with $Re_2(H)_8(PPh_3)_4$. We now report results of these studies on **1** and other related Au_2Re_2 clusters.

Experimental Section

Physical Measurements and Reagents. ^1H and ^{31}P NMR spectra were recorded at 300 and 121.5 MHz, respectively, with the use of a Nicolet NT-300 spectrometer. ^{31}P NMR spectra were run with proton decoupling and are reported in ppm relative to the external standard H_3PO_4 (85%), unless otherwise noted, with positive shifts downfield. All FABMS experiments were carried out with the use of a VG Analytical, Ltd., 7070E-HF high-resolution double-focusing mass spectrometer equipped with a VG 11/250 data system. A *m*-nitrobenzyl alcohol (MNBA) matrix was used, and experiments were run as described elsewhere.[4] UV-vis spectra were recorded with the use of a Hewlett-Packard 8451 diode array spectrometer. Conductivity measurements were made with the use of a Yellow Springs Model 31 conductivity bridge. Compound concentrations used in the conductivity experiments were 3×10^{-4} M in CH_3CN. Magnetic susceptibility measurements were made by the Faraday technique with use of $Hg[Co(SCN)_4]$ as calibrant. All solvents were reagent grade. CH_2Cl_2 was distilled from P_2O_5 and THF; 1,2-dimethoxyethane (DME) and toluene were distilled from sodium benzophenone ketyl. $[Au_2Re_2(H)_6(PPh_3)_6]^+$ (**1**),[4] $Au(PPh_3)NO_3$,[28]

---

(1) Mueting, A. M.; Bos, W.; Alexander, B. D.; Boyle, P. D.; Casalnuovo, J. A.; Balaban, S.; Ito, L. N.; Johnson, S. M.; Pignolet, L. H. Recent Advances in Di- and Polynuclear Chemistry. *New J. Chem.*, in press. See the references cited therein.

(2) Alexander, B. D.; Johnson, B. J; Johnson, S. M.; Boyle, P. D.; Kann, N. C.; Mueting, A. M.; Pignolet, L. H. *Inorg. Chem.* **1987**, *26*, 3506.

(3) Alexander, B. D.; Boyle, P. D.; Johnson, B. J; Johnson, S. M.; Casalnuovo, J. A.; Mueting, A. M.; Pignolet, L. H. *Inorg. Chem.* **1987**, *26*, 2547.

(4) 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. *Inorg. Chem.* **1987**, *26*, 1346.

(5) Alexander, B. D.; Johnson, B. J.; Johnson, S. M.; Casalnuovo, A. L.; Pignolet, L. H. *J. Am. Chem. Soc.* **1986**, *108*, 4409 and references cited therein.

(6) Boyle, P. D.; Johnson, B. J.; Buehler, A.; Pignolet, L. H. *Inorg. Chem.* **1986**, *25*, 5.

(7) Casalnuovo, A. L.; Laska, T.; Nilsson, P. V.; Olofson, J.; Pignolet, L. H. *Inorg. Chem.* **1985**, *24*, 233.

(8) Casalnuovo, A. L.; Laska, T.; Nilsson, P. V.; Olofson, J.; Pignolet, L. H.; Bos, W.; Bour, J. J.; Steggerda, J. J. *Inorg. Chem.* **1985**, *24*, 182.

(9) Casalnuovo, A. L.; Casalnuovo, J. A.; Nilsson, P. V.; Pignolet, L. H. *Inorg. Chem.* **1985**, *24*, 2554.

(10) Casalnuovo, A. L.; Pignolet, L. H.; van der Velden, J. W. A.; Bour, J. J.; Steggerda, J. J. *J. Am. Chem. Soc.* **1983**, *105*, 5957.

(11) Bos, W.; Steggerda, J. J.; Shiping, Y.; Casalnuovo, J. A.; Mueting, A. M; Pignolet, L. H. *Inorg. Chem.* **1988**, *27*, 948.

(12) Bour, J. J; Kanters, R. P. F.; Schlebos, P. P. J.; Bos, W.; Bosman, W. P.; Behm, H.; Beurskens, P. T.; Steggerda, J. J. *J. Organomet. Chem.* **1987**, *329*, 405.

(13) Jones, P. G. *Gold Bull.* **1986**, *19*, 46 and references cited therein.

(14) Braunstein, P.; Rosé, J. *Gold Bull.* **1985**, *18*, 17.

(15) Hall, K. P.; Mingos, D. M. P. *Prog. Inorg. Chem.* **1984**, *32*, 237 and references cited therein.

(16) Jones, P. G. *Gold Bull.* **1983**, *16*, 114 and references cited therein.

(17) Mingos, D. M. P.; Wardle, R. W. M. *J. Chem. Soc., Dalton Trans.* **1986**, 73.

(18) Gilmour, D. I.; Mingos, D. M. P. *J. Organomet. Chem.* **1986**, *302*, 127 and references cited therein.

(19) Briant, C. E.; Gilmour, D. I.; Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1986**, 835.

(20) Lauer, J. W.; Wald, K. *J. Am. Chem. Soc.* **1981**, *103*, 7648.

(21) Braunstein, P.; Lehner, H.; Matt, D.; Tiripicchio, A.; Tiripicchio-Camellini, M. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 304 and references cited therein.

(22) Johnson, B. F. G.; Lewis, J.; Nelson, W. J. H.; Raithby, P. R.; Vargas, M. D. *J. Chem. Soc., Chem. Commun.* **1983**, 608.

(23) Farrugia, L. J.; Freeman, M. J.; Green, M.; Orpen, A. G.; Stone, F. G. A.; Salter, I. D. *J. Organomet. Chem.* **1983**, *249*, 273.

(24) Braunstein, P.; Rose, J.; Manotti-Lanfredi, A. M.; Tiripicchio, A.; Sappa, E. *J. Chem. Soc., Dalton Trans.* **1984**, 1843.

(25) Johnson, B. F. G.; Kaner, D. A.; Lewis, J.; Raithby, P. R.; Taylor, M. J. *Polyhedron* **1982**, *1*, 105.

(26) Sutherland, B. R.; Ho, D. M.; Huffman, J. C.; Caulton, K. G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 135.

(27) Moehring, G. A.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1987**, *26*, 1861.

0020-1669/88/1327-4424$01.50/0

$[(Ph_3PAu)_3O]BF_4$,[29] $Re_2(H)_8(PPh_3)_4$,[30] $[Fe(C_5H_5)_2]PF_6$,[31] and (PPN)NO_3[32] (PPN = (μ-nitrido)bis(triphenylphosphorus)(1+)) were prepared by previously published procedures. Potassium *tert*-butoxide and tetrafluoroboric acid–diethyl ether were used as received from Aldrich. Tetrabutylammonium hexafluorophosphate (Southwestern Analytical Chemicals, Inc.) and CH_2Cl_2 (Burdick and Jackson Laboratories, Inc.) were used in the electrochemical experiments without further purification. All syntheses were carried out under a purified N_2 atmosphere with the use of standard Schlenk techniques, unless otherwise noted.

Electrochemistry. Electrochemical experiments were performed with a Bioanalytical Systems Model BAS-100 electrochemical analyzer at ambient temperature. A three-electrode configuration was used, which consisted of a highly polished glassy-carbon electrode (area 0.07 cm^2), a platinum spiral auxiliary electrode, and a Ag/AgCl reference electrode containing 1.0 M KCl. The working compartment of the electrochemical cell was separated from the auxiliary compartment by a fritted-glass salt bridge and from the reference compartment by a modified Luggin capillary. All of these compartments contained a 0.1 M solution of the supporting electrolyte tetrabutylammonium hexafluorophosphate (TBAH) in spectral grade CH_2Cl_2. Electrolyte solutions were prepared and stored over 80–200 mesh activated alumina and 4-Å molecular sieves prior to use. Working solutions were prepared by recording background cyclic voltammograms of 25 mL of the electrolyte solution before adding the sample of interest. The maximum scan range used for the cyclic voltammogram studies was from −1.8 to +1.8 V. Solvent-saturated argon was bubbled through the solution in the working compartment of the cell to deaerate the solution. Potentials were measured relative to an uncorrected Ag/AgCl reference electrode. No *iR* compensation was used.[33] Ferrocene was used as an internal standard to enable future corrections for the junction potentials. The ferrocene/ferrocenium couple for this electrochemical cell was 0.460 V in CH_2Cl_2/TBAH.[34]

Spectroelectrochemistry. The spectroelectrochemical experiments were performed by using a locally prepared optically transparent thin-layer electrode (OTTLE) cell and a Tracor TN-6500 diode array spectrometer. The OTTLE cell was prepared from a modified infrared solution cell. The working and pseudoreference electrodes were prepared by the vacuum deposition of thin layers of Pt metal onto quartz windows, and a Pt wire served as an auxiliary electrode. The path length of the cell was 0.2 mm. A Xe arc lamp served as the source of illumination, and the 512-element diode array was calibrated by using a holmium oxide standard. Solutions were prepared and degassed under an inert atmosphere (N_2 or Ar) and introduced into the OTTLE cell via a gastight syringe through polyethylene tubing. The spectra were acquired every 2–4 s by using 1 scan per spectrum. After the electrolysis, fresh solution was syringed into the cell and the electrolyzed material was flushed out through the outlet port.

Preparation of Compounds. $[Au_2Re_2(H)_6(PPh_3)_6](PF_6)_2$ (2(PF$_6$)$_2$). The blue-green paramagnetic cluster **1**(PF_6) (83.1 mg, 3.34 × 10^{-2} mmol) was dissolved in 5 mL of freshly distilled CH_2Cl_2. $[Fe(C_5H_5)_2]PF_6$ (11.2 mg, 3.38 × 10^{-2} mmol) was also dissolved in 5 mL of freshly distilled CH_2Cl_2. Upon addition of the ferrocenium solution to the cluster solution, the reaction mixture turned brownish red. The solvent volume was reduced in vacuo to ca. 5 mL, followed by the addition of Et_2O, which resulted in the formation of a red-brown precipitate. The solid was collected on a frit, washed with Et_2O, and dried under a steam of N_2; yield 75.7 mg, 86%. ^{31}P NMR (CH_2Cl_2, 22 °C): δ 73.0 (broad), 28.4 (broad). ^1H NMR (CD_2Cl_2, 25 °C, hydride region): δ −2.94, −3.42, −4.20 (ill-resolved multiplets). The equivalent conductance (164 cm^2 mho mol^{-1}) is indicative of a 2:1 electrolyte in CH_3CN solution. FABMS: *m/z* 2346 ($[Au_2Re_2(H)_6(PPh_3)_6]^+$ = (M)$^+$). UV–vis (λ (nm), log ϵ): 384, 3.85; 471, 3.77. Magnetic susceptibility measurements indicated the presence of a paramagnetic impurity.

$Au_2Re_2(H)_6(PPh_3)_6$ (3). Method i. A flask was charged with **1**(PF_6) (40.1 mg, 1.61 × 10^{-2} mmol) and KO^t*Bu* (78.0 mg, 0.695 mmol). Freshly distilled THF (8 mL) was added to the mixture and the solution allowed to stir for ca. 1 h, during which time the color changed from green-blue to red-brown. Following this, the THF was completely removed in vacuo, and the residue was extracted with freshly distilled toluene and the solution filtered. The toluene was removed in vacuo. Due to the air sensitivity of this material, no attempt was made to remove it from the flask for weighing.

Method ii. To a suspension of **1**(PF_6) (146.8 mg, 5.893 × 10^{-2} mmol) in 7 mL of freshly distilled THF was added 0.2 mL of a 0.37 M sodium naphthalenide solution (54% DME, 46% THF). The solution turned red-brown and was allowed to stir for 45 min. The solvents were removed in vacuo, and the solid residue was extracted with freshly distilled toluene.

From these reactions two closely related compounds (**3a**,**b**) could be isolated. Compound **3a** was the most readily isolated and characterized. ^{31}P NMR (toluene, 25 °C): δ 71.5, 43.1. ^1H NMR (toluene-d_8, 25 °C, hydride region): δ −4.39 (complex multiplet, J = 21.1 Hz, intensity 2), −6.75 (complex multiplet, J = 10.1 Hz, intensity 1). Compound **3b** was not consistently isolated; however, the following spectroscopic data was collected. ^{31}P NMR (toluene, 25 °C): δ 71.6, 43.2, −4.6 (very low intensity signal). ^1H NMR (toluene-d_8, 22 °C, hydride region): δ −3.36 (complex multiplet), −5.72 (poorly resolved multiplet); broad impurity peak at δ −5.05.

$[Au_2Re_2(H)_8(PPh_3)_6](BF_4)_2$ (4(BF$_4$)$_2$). An excess of $HBF_4 \cdot Et_2O$ (1.3 mL) was added to a toluene solution of **3**, which was prepared according to method i (vide supra) using 146.8 mg (5.893 × 10^{-2} mmol) of **1**(PF_6). This resulted in the formation of an oil. The solvents were removed in vacuo, and the solid residue was extracted with CH_2Cl_2. Addition of Et_2O resulted in a light rust brown precipitate, which was collected on a frit and washed with Et_2O; yield 113.9 mg, 76.6%. Attempted recrystallization from CH_2Cl_2/Et_2O resulted in decomposition to $[Au_2Re_2(H)_7(PPh_3)_6]^+$, $[Au(PPh_3)_2]^+$, and other uncharacterized phosphorus-containing product(s). ^{31}P NMR (CH_2Cl_2, 22 °C): δ 66.9, 25.7; broad side product resonances at δ 73.4 and 28.5. ^1H NMR (CD_2Cl_2, 22 °C, hydride region): δ −2.75 (ill-resolved multiplet). FABMS: *m/z* 2346 ((M − 2H)$^+$ where M = $[Au_2Re_2(H)_8(PPh_3)_6]$).

$[Au_2Re_2(H)_7(PPh_3)_6]BF_4$ (5(BF$_4$)). A flask was charged with 70.0 mg (4.73 × 10^{-2} mmol) of $[(Ph_3PAu)_3O]BF_4$ and 85.2 mg (5.96 × 10^{-2} mmol) of $Re_2(H)_8(PPh_3)_4$ and degassed. Freshly distilled CH_2Cl_2 (5 mL) was added to the flask, and immediately a dark red solution formed. Et_2O was added, precipitating a red-brown solid. The solid was filtered and washed with Et_2O, yielding 100.0 mg of this material. The mother liquor was still colored, and subsequent analysis showed the color of the ether-soluble fraction to be due to $AuRe_2(H)_7(PPh_3)_5$.[15] ^{31}P NMR (CD_2Cl_2, 22 °C): δ 69.2 (s, Au*P*), 31.8 (s, Re*P*). ^1H NMR (CD_2Cl_2, 22 °C, hydride region): δ −3.03 (p of t, $J_{P_{Au}-H}$ = 9.6 Hz, $J_{P_{Re}-H}$ = 5.7 Hz). FABMS: *m/z* 2347 ($[Au_2Re_2(H)_7(PPh_3)_6]^+$ = (M)$^+$). UV–vis (λ (nm), log ϵ): 337 (sh), 4.15; 502, 3.43. Anal. Calcd for $Re_2Au_2P_6C_{108}H_{97}BF_4$: C, 53.29; H, 4.02; P, 7.63. Found: C, 52.98; H, 4.12; P, 7.52.

Reaction of $[Au_2Re_2(H)_6(PPh_3)_6](PF_6)_2$ (2(PF$_6$)$_2$) with H$_2$. **2**(PF_6)$_2$ (51.2 mg, 1.94 × 10^{-2} mmol) was dissolved in 7 mL of freshly distilled THF and the solution exposed to 1 atm of H_2. Within 1 h the solution color changed from brown-red to blue-green, and upon addition of Et_2O a blue-green precipitate was formed. This solid was collected on a frit and washed with Et_2O. ^{31}P NMR (CH_2Cl_2, 22 °C, trimethyl phosphate (TMP) internal standard): δ 66.9, 29.5 ($[Au_2Re_2(H)_7(PPh_3)_6]^+$ (**5**)); unassigned side product at δ 42.2. The TMP peak was broad. The UV–vis spectrum of the product matched that of an authentic sample of $[Au_2Re_2(H)_6(PPh_3)_6]^+$ (**1**).

Reaction of $[Au_2Re_2(H)_8(PPh_3)_6](BF_4)_2$ (4(BF$_4$)$_2$) with (PPN)NO$_3$. **4**(BF_4)$_2$ (13.9 mg, 5.51 × 10^{-3} mmol) was dissolved in 10 mL of freshly distilled CH_2Cl_2 along with 2 equiv of (PPN)NO_3 (6.8 mg, 0.011 mmol). Within several minutes the red-brown solution changed to the distinctive blue-green color of the paramagnetic cluster ion $[Au_2Re_2(H)_6(PPh_3)_6]^+$ (**1**), as observed by UV–vis spetroscopy. ^{31}P NMR spectrum of the resulting solution (CH_2Cl_2, 22 °C): δ 42.2 (broad), 27.7, 21.6 (PPN$^+$).

Reaction of $Au_2Re_2(H)_6(PPh_3)_6$ (3) with (PPN)NO$_3$ in Acidic Media. A solution of **3** was generated from 25.6 mg (1.03 × 10^{-2} mmol) of **1**(PF_6) by using method i (vide supra). The toluene was removed in vacuo, and the resulting residue was dissolved in 3 mL of freshly distilled THF. A solution of (PPN)NO_3 (12.9 mg, 2.15 × 10^{-2} mmol) dissolved in 5 mL of THF was added to the solution of **3** with no observable color change. Upon addition of 0.2 mL of $HBF_4 \cdot Et_2O$ the solution changed immediately from brown to the distinctive blue-green color of the paramagnetic hexahydride cluster $[Au_2Re_2(H)_6(PPh_3)_6]^+$ (**1**), which was confirmed by the UV–vis spectrum of this in situ reaction mixture.

Reaction of $[Au_2Re_2(H)_7(PPh_3)_6]BF_4$ (5(BF$_4$)) with KO^{t}Bu. A flask was charged with **5**(BF_4) (22.8 mg, 9.37 × 10^{-3} mmol) and KO^{t}Bu (29.8 mg, 0.265 mmol). Freshly distilled THF (5 mL) was added to this flask. The reaction mixture was allowed to stir for 1 h, at which time the solvent was removed in vacuo. The resultant residue was extracted with toluene-d_8 and the extract transferred to an NMR tube for the acquisition of the ^{31}P and ^1H NMR spectra. ^{31}P NMR (toluene-d_8, 22 °C): δ 71.6,

---

(28) Malatesta, L.; Naldini, L.; Simonetta, G.; Cariati, F. *Coord. Chem. Rev.* **1966**, *1*, 255.

(29) Nesmeyanov, A. N.; Perevalova, E. G.; Struchkov, Yu. T.; Antipin, M. Yu.; Grandberg, K. I.; Dyadchenko, V. P. *J. Organomet. Chem.* **1981**, *201*, 343.

(30) Chatt, J.; Coffey, R. S. *J. Chem. Soc. A* **1969**, 1963.

(31) Nesmeyanov, A. N.; Materikova, R. B.; Lyatifov, I. R.; Kurbanov, T. Kh.; Kochetkova, N. S. *J. Organomet. Chem.* **1978**, *145*, 241.

(32) Martinsen, A.; Songstad, J. *Acta Chem. Scand., Ser. A* **1977**, *A31*, 645.

(33) Gagne, R. R.; Koval, C. A.; Kisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854.

(34) $E°$ for the FeCp$^+$/FeCp$_2$ couple is +0.400 V vs NHE in H_2O solutions. See: Koepp, H. M; Wendt, H.; Strehlow, H. Z. *Z. Elektrochem.* **1960**, *64*, 483.

43.2 ($Au_2Re_2(H)_6(PPh_3)_6$); other unassigned signals at δ 75.0, 42.7, 32.8. ^1H NMR (toluene-d_8, 22 °C, hydride region): δ −3.34 (mult), −5.73 (mult, $Au_2Re_2(H)_6(PPh_3)_6^+$); other unassigned signals at δ −2.86 (broad), −5.03 (broad).

Reaction of $[Au_2Re_2(H)_7(PPh_3)_6]BF_4$ (5(BF_4)) with $[Fe(C_5H_5)_2]PF_6$. A flask was charged with **5**(BF_4) (35.8 mg, 1.47 × 10^{-2} mmol) and $[Fe(C_5H_5)_2]PF_6$ (4.8 mg, 1.45 × 10^{-2} mmol). CH_2Cl_2 (2 mL) was added to this mixture with the immediate formation of a blue solution. After the solution was stirred for several minutes, diethyl ether was added and a precipitate formed. The precipitate was collected by filtration and washed with Et_2O; yield 33.2 mg of $[Au_2Re_2(H)_7(PPh_3)_6](BF_4)(PF_6)$. FABMS: *m/z* 2347 ($[Au_2Re_2(H)_7(PPh_3)_6]^+ = (M)^+$). UV–vis (λ nm), log ε): 505, 3.57; 604, 3.6.

Reaction of $[Au_2Re_2(H)_7(PPh_3)_6](BF_4)(PF_6)$ with H_2. $[Au_2Re_2(H)_7(PPh_3)_6](BF_4)(PF_6)$ (19.5 mg, 7.56 × 10^{-3} mmol) was dissolved in CH_3CN (2 mL) and the solution allowed to stir under 1 atm of H_2 for 3 h. A brown precipitate formed upon the addition of 5 mL of Et_2O. The UV–vis spectrum of this solid matched that of an authentic sample of **5**.

Results and Discussion

Synthetic Aspects. Work has recently been carried out in this area on related gold–rhenium systems by Walton[27] and Caulton.[26] Their work complements the present study and highlights the importance of the role of the anion in the chemistry of these compounds (vide infra). For example, Walton reported the reaction between $Re_2(H)_8(PPh_3)_4$ and "$AuPPh_3^+$", generated in situ from $Au(PPh_3)Cl$ and $AgPF_6$. The products of this reaction were $[AuRe_2(H)_8(PPh_3)_5]^+$ and $[Au_2Re_2(H)_8(PPh_3)_6]^{2+}$, which resulted from of the addition of one or two gold(I) phosphine cations, respectively, with no loss of H^+. Caulton has carried out a similar reaction starting with $Re_2(H)_8(PMe_2Ph)_4$ and the gold(I) alkoxide Ph_3PAuO^tBu. In this case the loss of two H^+ ions occurred along with the addition of two gold(I) phosphine cations, yielding two isomers of $Au_2Re_2(H)_6(PMe_2Ph)_4(PPh_3)_2$. In both of these reactions only diamagnetic products were reported to have been isolated.

We have previously reported that the reaction of $Re_2(H)_8(PPh_3)_4$ with 2 equiv of $Au(PPh_3)NO_3$ in CH_2Cl_2 solutions leads to the formation of the green paramagnetic cluster complex $[Au_2Re_2(H)_6(PPh_3)_6]^+$ (**1**).[4] The formation of this complex involved the formal replacement of two H^+ ions by two $AuPPh_3^+$ cations accompanied by a one-electron oxidation. Examination of the in situ reaction mixture at low temperature by ^{31}P NMR spectroscopy provided information about intermediates involved in the formation of this paramagnetic mixed-metal cluster complex. At −30 °C the ^{31}P NMR spectrum displayed resonances due to $[Au_2Re_2(H)_8(PPh_3)_6]^{2+}$ (**4**) and $[Au_2Re_2(H)_7(PPh_3)_6]^+$ (**5**), which have been previously synthesized and characterized by Walton.[27] Upon warming to 0 °C, the solution turned from red to green, which indicated the formation of the paramagnetic cluster, **1**. The ^{31}P NMR spectrum at 0 °C showed only resonances due to an unidentified ether-soluble product and compound **5**. Complex **5** was always observed as a minor impurity in isolated solid samples of **1**. Complex **1** did not display a ^{31}P NMR spectrum due to its paramagnetic nature. These results are shown in the following equations and suggest that complex **4** is formed first and then oxidized to give the $[Au_2Re_2(H)_6(PPh_3)_6]^+$ cluster:

$$Re_2(H)_8(PPh_3)_4 + 2Au(PPh_3)NO_3 \xrightarrow[CH_2Cl_2]{-30\ ^\circ C}$$

$$\underset{\mathbf{4}}{[Au_2Re_2(H)_8(PPh_3)_6]^{2+}} + \underset{\mathbf{5}}{[Au_2Re_2(H)_7(PPh_3)_6]^{+}}$$

$$\Big\downarrow 0\ ^\circ C$$

$$\underset{\mathbf{1}}{[Au_2Re_2(H)_6(PPh_3)_6]^{+}}$$

Further support for this was obtained from the reaction of isolated complexes $Au_2Re_2(H)_6(PPh_3)_6$ (**3**) and $[Au_2Re_2(H)_8(PPh_3)_6]^{2+}$ (**4**) with NO_3^- (vide infra).

In the reaction of $Re_2(H)_8(PPh_3)_4$ with $[(Ph_3PAu)_3O]BF_4$, oxidation did not occur and only the diamagnetic complex $[Au_2Re_2(H)_7(PPh_3)_6]^+$ (**5**) was formed. The ^{31}P and ^1H NMR spectra of the complex isolated from this reaction were in agreement with those previously published for **5**, which was synthesized from $AuRe_2(H)_7(PPh_3)_5$ and in situ generated $AuPPh_3^+$.[27] Resonances in the ^{31}P NMR spectrum were assigned by comparing the chemical shifts to those of other Au–Re clusters.[3,4,6,26,27,35] Thus, the peak at δ 69.2 is due to the gold phosphines and the resonance at δ 31.8 is assigned to the rhenium phosphines. Selective ^{31}P decoupling of the hydride signals of **5** showed the hydride multiplet at δ −3.30 collapses to a pentet from the decoupling of the Au*P* resonance at δ 69.2 and to a triplet from the decoupling of the Re*P* resonance at δ 31.8, confirming the formulation of the cluster as having a $Re_2P_4(AuP)_2$ framework. FABMS also showed a parent peak at *m/z* 2347 with the correct mass and isotopic pattern, which further supports the formulation of **5** as $[Au_2Re_2(H)_7(PPh_3)_6]^+$ (Experimental Section).

The above reaction is interesting since Walton reported that $Re_2(H)_8(PPh_3)_4$ reacted with 1 equiv of "$AuPPh_3^+$", generated in situ from $Au(PPh_3)Cl$ and $AgPF_6$, to give $[Au_2Re_2(H)_8(PPh_3)_6]^{2+}$ (**4**).[27] The isolation of $[Au_2Re_2(H)_7(PPh_3)_6]^+$ (**5**) instead of **4** from the reaction of $Re_2(H)_8(PPh_3)_4$ with $[(Ph_3PAu)_3O]BF_4$ is probably associated with the ability of the oxide to act as a base whereas PF_6^- could not perform effectively as a deprotonating agent. This argument is somewhat speculative since the formulation of the in situ formed "$Au(PPh_3)PF_6$" is not known; however, it is clear that the anion is very important in these reactions. Furthermore, Caulton used gold(I) phosphine *tert*-butoxide, a starting material with an even more basic ancillary ligand that produced an analogue of complex **3**, $Au_2Re_2(H)_6(PPh_3)_2(PMe_2Ph_3)_4$,[26] the doubly deprotonated form of the diamagnetic Au_2Re_2 clusters.[26] The effect of the nitrate anion is also apparent in the synthesis of $[Au_2Re_2(H)_6(PPh_3)_6]^+$ (**1**) from $Au(PPh_3)NO_3$ and $Re_2(H)_8(PPh_3)_4$. In this case NO_3^- also functions as an oxidizing agent (vide infra). These reactions are summarized as follows and in Figure 1:

$$Re_2(H)_8(PPh_3)_4 + \text{"}Au(PPh_3)PF_6\text{"} \xrightarrow[CH_2Cl_2/acetone]{} \underset{\mathbf{4}}{[Au_2Re_2(H)_8(PPh_3)_6]^{2+}} + [AuRe_2(H)_8(PPh_3)_5]^+$$

$$Re_2(H)_8(PPh_3)_4 + [(Ph_3PAu)_3O]BF_4 \xrightarrow[CH_2Cl_2]{} \underset{\mathbf{5}}{[Au_2Re_2(H)_7(PPh_3)_6]^+}$$

$$Re_2(H)_8(PMe_2Ph)_4 + 2[Ph_3PAuO^tBu] \xrightarrow[C_6H_6]{} Au_2Re_2(H)_6(PMe_2Ph)_4(PPh_3)_2$$

$$Re_2(H)_8(PPh_3)_4 + 2Au(PPh_3)NO_3 \xrightarrow[CH_2Cl_2]{0\ ^\circ C} \underset{\mathbf{1}}{[Au_2Re_2(H)_6(PPh_3)_6]^+} + \underset{\mathbf{5}}{[Au_2Re_2(H)_7(PPh_3)_6]^+}$$

Spectral and Magnetic Properties of $[Au_2Re_2(H)_6(PPh_3)_6]^+$. The paramagnetism of **1** was confirmed by magnetic susceptibility and electron spin resonance (ESR) measurements. The magnetic moment of 1.77 μ_B indicated one unpaired electron in this compound. The ESR spectrum of **1** (Figure 2) is somewhat similar to that of $[Re_2(H)_8(PPh_3)_4]^+$.[36] The spectrum of complex **1** obtained in frozen CH_2Cl_2 at 9.4 K showed a nearly featureless signal centered at a *g* value of 2.18 with an approximate hyperfine coupling constant of 110 G. The ESR spectrum of $[Re_2(H)_8(PPh_3)_4]^+$ showed an 11-line pattern centered at $g = 2.16$ with a hyperfine coupling constant in the range 140–150 G.

Electrochemical Studies. Cyclic voltammetric studies on $[Au_2Re_2(H)_6(PPh_3)_6]^+$ (**1**), as the PF_6^- salt, and $[Au_2Re_2(H)_7(PPh_3)_6]^+$ (**5**), as the BF_4^- salt, revealed interesting electrochemical properties. The cyclic voltammogram of **1** (Figure 3) showed a quasi-reversible oxidation (+1/+2 couple) at $E_{1/2}$ = 67 mV and a quasi-reversible reduction (+1/0 couple) at $E_{1/2}$ = −713 mV. The quasi-reversible designation for these processes is based on

---

[35] Sutherland, B. R.; Folting, K.; Streib, W. E.; Ho, D. M.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1987**, *109*, 3489.

[36] Allison, J. D.; Cameron, C. J.; Wild, R. E.; Walton, R. A. *J. Organomet. Chem.* **1981**, *218*, C62.

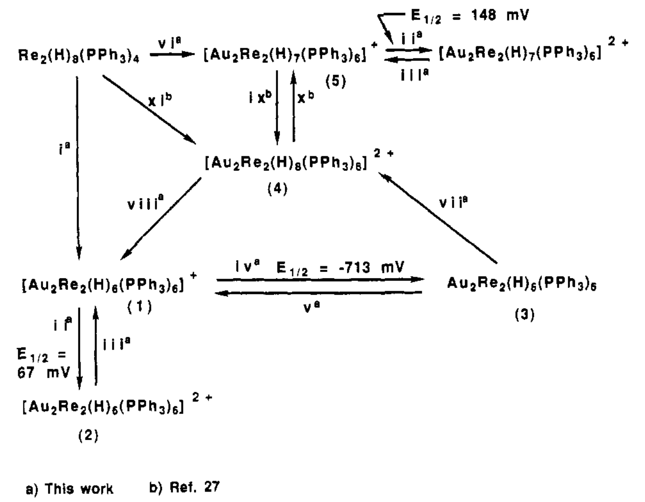

Figure 1. Reaction scheme for the synthesis and interconversion of $[Au_2Re_2(H)_x(PPh_3)_6]^{n+}$ cluster compounds. Conditions: (i) $2Au(PPh_3)NO_3$ in CH_2Cl_2, -30 °C; (ii) $Cp_2Fe(PF_6)$ in CH_2Cl_2; (iii) H_2, THF; (iv) $Na(C_{10}H_8)$ in DME/THF or KO^tBu in THF; (v) $(PPN)NO_3$ and $HBF_4{\cdot}Et_2O$ in THF; (vi) $^2/_3[(Ph_3PAu)_3O]BF_4$ in CH_2Cl_2; (vii) excess $HBF_4{\cdot}Et_2O$ in toluene; (viii) $(PPN)NO_3$ in CH_2Cl_2; (ix) $HBF_4{\cdot}Et_2O$ in CH_2Cl_2; (x) Et_3N in CH_3OH, CH_3CH_2OH, or acetone; (xi) $Au(PPh_3)Cl$ and $AgPF_6$ in CH_2Cl_2/acetone. Potentials were measured vs Ag/AgCl in CH_2Cl_2/TBAH (0.1 M).

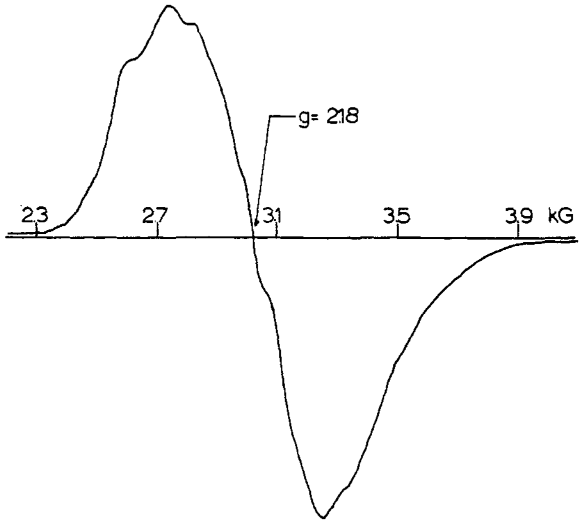

Figure 2. ESR spectrum of $[Au_2Re_2(H)_6(PPh_3)_6]PF_6$ in CH_2Cl_2 glass at 9.4 K.

several observations: (i) the peak separations ($E_{p,c} - E_{p,a}$) of ca. 85 mV (the peak separation for the ferrocene/ferrocenium couple under these conditions is ca. 150 mV at a scan rate of 100 mV/s); (ii) the observation of peak current ratios near unity for both waves ($i_{p,c}/i_{p,a} \approx 1$); (iii) the linear response of a plot of $i_{p,a}$ vs $v^{1/2}$ over the range of scan rates investigated. Anson plots prepared from chronocoulometric data yielded comparable slopes for the redox processes, which indicates that the transitions involve the same number of electrons. Attempts to prepare the oxidized species, **2**, by bulk electrolysis proved unsuccessful due to the long-term instability of the oxidized species.

Spectroelectrochemical studies were performed on both the anodic and cathodic waves of **1**(PF_6). The spectral changes observed upon oxidation at 300 mV (Figure 4) showed two isosbestic points at 551 and 406 nm, indicating the clean conversion of **1** to the oxidized species, $[Au_2Re_2(H)_6(PPh_3)_6]^{2+}$ (**2**). The bands for the starting material at 615, 462 (shoulder), and 338 (shoulder) nm disappeared as the electrolysis progressed and new bands at 395 and 482 nm appeared. The spectral changes upon cathodic electrolysis at -1.0 V, however, did not produce a clearly defined isosbestic point nor a distinctive spectrum for the reduced species.

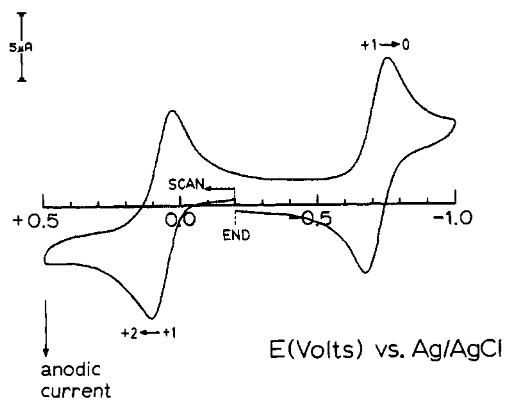

Figure 3. Cyclic voltammogram of $[Au_2Re_2(H)_6(PPh_3)_6]PF_6$ (**1**(PF_6)) in CH_2Cl_2/0.1 M TBAH (Ag/AgCl reference electrode; scan rate 100 mV/s).

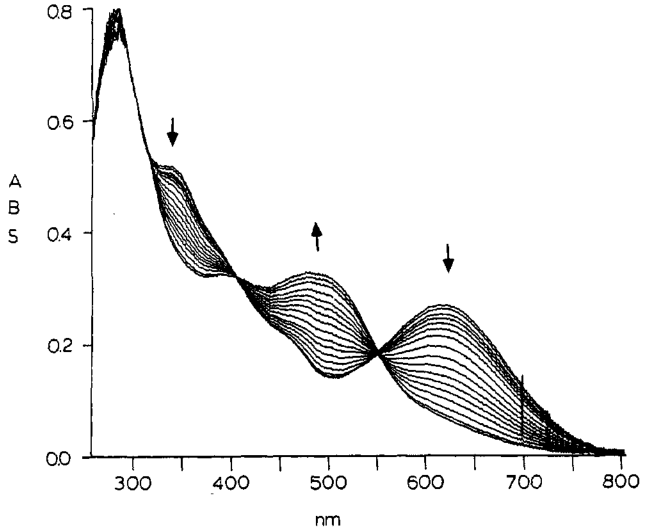

Figure 4. UV–vis spectroelectrochemistry of anodic electrolysis of $[Au_2Re_2(H)_6(PPh_3)_6]PF_6$ in 3.3×10^{-3} M CH_2Cl_2/0.1 M TBAH.

The cyclic voltammogram of **5** exhibited an irreversible oxidation at 970 mV and a quasi-reversible oxidation (+1/+2 couple) at $E_{1/2}$ = 148 mV ($i_{p,c}/i_{p,a}$ = 1.1 and $E_{p,c} - E_{p,a}$ = 75 mV). Spectroelectrochemical studies showed the clean conversion of **5** to its oxidized form upon oxidation at 500 mV (see supplementary material for the results of these experiments). As the electrolysis proceeded, the shoulder at 337 nm due to **5** disappeared, and an extremely broad band centered at 600 nm appeared. After the electrolysis was complete, the final spectrum agreed well with the UV–vis spectrum of an authentic sample of the oxidized form of **5** prepared chemically by the reaction of **5** with ferrocenium. Exposure of a CH_3CN solution of this oxidized form of **5** to H_2 regenerated the original cluster complex, **5**, (vide infra).

The electrochemical properties of the Au_2Re_2 clusters are similar to those of the $AuRe_2$ clusters and $[Re_2(H)_8(PPh_3)_4]^+$. The peak separations and peak current ratios in all these compounds are comparable. While the number of gold atoms in the cluster affects the potentials for the redox processes, the reversibility of the electron-transfer processes is not greatly affected.

Chemical Redox Reactions and Isolation of Products. The oxidized and reduced species observed in the cyclic voltammetric experiments of **1** were chemically prepared and isolated. The reactions used to produce these compounds and to convert them into other members of the Au_2Re_2 family are shown in Figure 1 and detailed in the Experimental Section. The oxidation of **2** was accomplished by the addition of ferrocenium to **1**(PF_6) in CH_2Cl_2, resulting in a color change of green to red. Due to the presence of $[Au_2Re_2(H)_7(PPh_3)_6]^+$ (**5**) as an impurity in the starting material (vide supra), however, the formation of paramagnetic impurities in the product made characterization of this species by NMR spectroscopy difficult. The ^{31}P NMR spectrum at 22 °C with CH_2Cl_2 as solvent consisted of two broad resonances at δ 73.0 and 28.4. Magnetic susceptibility measurements indicated the presence of a paramagnetic impurity. The ^1H NMR spectrum in the hydride region showed ill-resolved multiplets at δ −2.94, −3.42, and −4.20. Attempts to purify **2** by recrystallization resulted in decomposition.

The FABMS data for **2** indicated the molecular weight of the cluster cation to be 2346, which corresponds to the formulation of this complex as a $[Au_2Re_2(H)_6(PPh_3)_6]^{n+}$ cluster. In accordance with our previous experience with FABMS of dicationic clusters, one might have expected to observe the ion pair $(M + X)^+$ peak in the spectrum;[1] however, this was not observed, nor was the $(M/2)^+$ peak. This could be due to the formation of easily oxidized matrix fragments during the bombardment process and the facile reduction of **2** to **1**. Similar reduction during FABMS has been observed in the FABMS spectrum of the oxidized form of **5**. Further support for the formulation of **2** comes from conductivity and UV–vis data. The equivalent conductance of 164 cm^2 mho mol^{-1} is indicative of a 2:1 electrolyte in CH_3CN. Additionally, the UV–vis spectrum of **2** produced chemically agreed well with the final spectrum obtained during electrochemical oxidation (Figure 2).

The chemical reduction of $\mathbf{1}(PF_6)$ was accomplished either by the addition of 1 equiv of sodium naphthalenide in a THF/DME mixture or by the addition of an excess of potassium *tert*-butoxide in THF, which can act as a reductant in anhydrous media.[37] The reduction with *tert*-butoxide was the method of choice due to convenience and the fact that the ever-present impurity $[Au_2Re_2(H)_7(PPh_3)_6]^+$ (**5**) was also deprotonated to give the desired product, which is formulated as $Au_2Re_2(H)_6(PPh_3)_6$ (**3**). Isolation of pure samples of **3** proved difficult due to the instability of the solid, which slowly turned green when exposed to air.

Examination of the ^{31}P NMR spectra of different preparations of **3** revealed that two closely related compounds, **3a** and **3b**, were produced in the reaction. This was not unexpected since Caulton had observed two isomers of the analogous compound $Au_2Re_2(H)_6(PPh_3)_2(PMe_2Ph)_4$.[26] The ^{31}P NMR spectrum of **3a** with toluene as solvent at room temperature showed two singlet resonances at δ 71.5 and 43.1. The ^1H NMR spectrum with toluene-d_8 as solvent showed a pseudosextet centered at δ −4.39 with an apparent coupling constant of 21.1 Hz and an ill-resolved multiplet at δ −6.75 (J = 10.1 Hz) with relative areas of 2:1. Selective ^{31}P decoupling of the signal at δ 71.5 caused the pseudosextet at δ −4.39 to collapse to a triplet (J = 31.7 Hz) and the multiplet at δ −6.75 to remain unaffected. Decoupling of the δ 43.1 resonance resulted in the collapse of the pseudosextet at δ −4.39 to a doublet (J = 21.2 Hz) and the multiplet at δ −6.75 to a singlet. On the basis of these data and the chemical shifts of the related compound $Au_2Re_2(H)_6(PPh_3)_2(PMe_2Ph)_4$,[26] the δ 71.5 resonance is assigned to the phosphines on the gold atoms and the δ 43.1 resonance to the rhenium phosphines. In the ^1H NMR spectrum, the δ −4.39 peak (intensity 2) is assigned to terminal hydrides and the δ −6.75 peak (intensity 1) to hydrides bridging the two rhenium atoms. These assignments are supported by the crystal structure of Caulton's symmetric isomer of $Au_2Re_2(H)_6(PPh_3)_2(PMe_2Ph)_4$,[26] which is analogous to **3a**.

Compound **3b** was not consistently observed in the synthesis of **3** by either method of preparation. Attempts to vary reaction conditions to increase the selectivity of the reaction of **3b** were unsuccessful. The ^{31}P NMR spectrum of **3b** displayed resonances at δ 71.6, 43.2, and −4.6. This was initially mistaken for the spectrum of **3a** because of the very low intensity of the δ −4.6 peak at room temperature. At −88 °C with all three peaks maintaining their sharpness, however, this resonance was of a much greater intensity. As the sample was warmed and monitored by ^{31}P NMR spectroscopy, the δ −4.6 resonance steadily decreased in intensity. At room temperature the interpulse delay time was increased from 0.3 to 5.0 s and the intensity of this peak doubled. This suggests that the low intensity of the δ −4.6 resonance is due to an atypical relaxation time. This upfield resonance is assigned to compound **3b** as a result of selective ^{31}P NMR decoupling experiments. The ^1H NMR spectrum showed a P–H coupling of 11.1 Hz not observed in **3a** due to coupling to the δ −4.6 phosphorus. This was observed upon decoupling of the δ 71.6 and 43.2 resonances. Due to the similar chemical shifts of **3b** and **3a**, the δ 71.6 and 43.2 resonances are assigned to Au*P* and Re*P*, respectively. Although the selective decoupling experiment indicated that the δ −4.6 resonance is due to **3b**, it cannot be unequivocally assigned as either Re*P* or Au*P*.

The reaction of **3** with an excess of $HBF_4 \cdot Et_2O$ in THF gave the previously characterized cluster compound $[Au_2Re_2(H)_8(PPh_3)_6]^{2+}$ (**4**). The ^{31}P and ^1H NMR chemical shifts are in good agreement with the values published by Walton.[27] Also present in the spectrum were minor peaks presumably due to $[Au_2Re_2(H)_6(PPh_3)_6]^{2+}$ (**2**). The FABMS data showed a peak at m/z 2346, assigned as $(M - 2H)^+$, which indicates the acidic nature of these hydride ligands.

The reaction of H_2 with $[Au_2Re_2(H)_6(PPh_3)_6]^{2+}$ (**2**) in THF regenerated the paramagnetic cluster compound, $[Au_2Re_2(H)_6(PPh_3)_6]^+$ (**1**). One might have expected the oxidative addition of H_2 to give **4**; however, this was not observed. This could be because the Re_2 core is already too electron deficient, making oxidative addition unfavorable. It is interesting to note that the reduction of **2** with H_2 proceeds quickly in THF and slowly or not at all in CH_2Cl_2, probably because the greater polarity of THF stabilizes the oxidation of H_2 to H^+. The ^{31}P NMR spectrum of the reaction mixture indicated that two minor diamagnetic products were also produced during this reaction. One of these is complex **5**, and the other is an impurity that has a chemical shift of δ 42.2 vs TMP in the ^{31}P NMR spectrum. In this reaction, **5** is formed from the H_2 reduction of the oxidized form of **5**, $[Au_2Re_2(H)_7(PPh_3)_6]^{2+}$. This oxidized form of **5** was produced in the original oxidation of the impure sample of $\mathbf{1}(PF_6)$ by ferrocenium (recall that $\mathbf{5}(PF_6)$ was always present as an impurity in the samples of **1**). The aforementioned ether-soluble product has not yet been identified for the reaction mixture in the preparation of **1**.

In a similar fashion, when CH_3CN solutions of $[Au_2Re_2(H)_7(PPh_3)_6]^{2+}$, the oxidized form of **5**, were exposed to H_2, the solution turned from blue purple to brown over the course of 3 h. Isolation of the product by precipitation with Et_2O and subsequent characterization by UV–vis spectroscopy showed the product to be **5**. This was confirmed by comparison to a spectrum of an authentic sample of **5**.

The reactions of $[Au_2Re_2(H)_8(PPh_3)_6]^{2+}$ (**4**) and $Au_2Re_2(H)_6(PPh_3)_6$ (**3**) with NO_3^- are important to demonstrate the noninnocence of the nitrate ligand in the formation of $[Au_2Re_2(H)_6(PPh_3)_6]^+$ (**1**). The addition of $(PPN)NO_3$ to a CH_2Cl_2 solution of **4** produced **1**, as shown by the UV–vis spectrum of the reaction mixture. This directly correlates with the earlier observation of the in situ variable-temperature ^{31}P NMR study of the reaction between $Re_2(H)_8(PPh_3)_4$ and $Au(PPh_3)NO_3$, which showed initial formation of **4** and **5** and subsequent oxidation of **4** to yield **1**. The addition of $(PPN)NO_3$ to a THF solution of **3** did not initially give a reaction. The subsequent addition of $HBF_4 \cdot Et_2O$, however, resulted in the oxidation of **3** to **1**. This reaction demonstrates that HNO_3 is the oxidant in the formation of **1**.

Walton has previously demonstrated the conversion of **4** to **5** by deprotonation with NEt_3. In a similar fashion, reaction of a THF solution of $\mathbf{5}(BF_4)$ with KO^tBu caused the deprotonation of **5** to yield **3**. This was confirmed by the ^{31}P and ^1H NMR spectra of the reaction mixture after extraction with toluene-d_8. There were other phosphorus-containing products formed; however, these remain uncharacterized.

Conclusion

The reaction of gold(I) phosphine compounds with $Re_2(H)_8(PPh_3)_4$ yields a novel family of mixed-metal cluster compounds containing rhenium and gold that have subtle acid–base and redox chemistries. The electrochemical properties of these clusters are similar to those of the parent complex, $Re_2(H)_8(PPh_3)_4$, indicating

---

[37] Russell, G. A.; Blankespoor, R. L. *Tetrahedron Lett.* **1971**, *47*, 4573.

that considerable multiple-bond character between the rhenium atoms is maintained in these mixed-metal cluster compounds. This is further supported by the fact that the ESR spectrum of $[Au_2Re_2(H)_6(PPh_3)_6]^+$ (**1**), with respect to *g* value and hyperfine coupling constants, is somewhat similar to that of the oxidized parent complex prepared by Walton.[36]

Comparison of the present work to the work of Caulton[26] and Walton[27] leads us to conclude that the starting gold(I) phosphine complex significantly affects the course of the reaction and determines the final product(s). If an acidic anion is used, then the fully protonated Au_2Re_2 cluster $[Au_2Re_2(H)_8(PPh_3)_6]^{2+}$ (**4**) is formed.[27] The use of counterions of varying basicity leads to clusters $Au_2Re_2(H)_6(PPh_3)_6$ (**3**) or $[Au_2Re_2(H)_7(PPh_3)_6]^+$ (**5**), in which all[26] or some of the hydride ligands with acidic character have been abstracted. This work shows the noninnocence of the NO_3^- ion in the formation of these gold–rhenium clusters. When present in a reaction mixture where H^+ is being generated, the NO_3^- ion can oxidize the clusters with accessible oxidation potentials.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE-851923) and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We gratefully acknowledge the Johnson Matthey Co. for a generous loan of gold salts.

Registry No. **1**(PF_6), 107712-43-6; **2**$(PF_6)_2$, 117226-13-8; **3a**, 117201-64-6; **3b**, 117201-65-7; **4**$(BF_4)_2$, 117201-66-8; **5**(BF_4), 117201-67-9; $[(Ph_3PAu)_3O]BF_4$, 53317-87-6; K(O-*t*-Bu), 865-47-4; $[Fe(C_5H_5)_2]PF_6$, 11077-24-0; $Re_2(H)_8(PPh_3)_4$, 66984-37-0; Re, 7440-15-5; Au, 7440-57-5; sodium naphthalenide, 3481-12-7.

Supplementary Material Available: Figures of cyclic voltammetric and spectroelectrochemical experiments on $[Au_2Re_2(H)_7(PPh_3)_6]^+$ (2 pages). Ordering information is given on any current masthead page.

Contribution from the Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione,
CNR, Via J. Nardi 39, 50132 Florence, Italy, Dipartimento di Chimica dell'Università di Siena,
53100 Siena, Italy, and Departamento de Quimica, Universidad de Valencia, Valencia, Spain

Synthesis, Characterization, and Electrochemical Properties of a Family of Dinuclear Rhodium Complexes Containing Two Terminal Hydride Ligands and Two Hydride (or Chloride) Bridges. Stoichiometric and Catalytic Hydrogenation Reactions of Alkynes and Alkenes

Claudio Bianchini,[*,1] Andrea Meli,[1] Franco Laschi,[2] José A. Ramirez,[3] Piero Zanello,[2]
and Alberto Vacca[1]

Received March 31, 1988

Protonation by strong acids and thermal decomposition in solution are two routes by which the trihydride (triphos)RhH_3 (**1**) [triphos = $MeC(CH_2PPh_2)_3$] is used to synthesize the tetrahydrido complexes $[(\text{triphos})RhH(\mu\text{-}H)_2HRh(\text{triphos})](BPh_4)_2$ (**2**) and $[(\text{triphos})RhH(\mu\text{-}H)_2HRh(\text{triphos})]$ (**3**), respectively. The bis(μ-chloro) dihydride $[(\text{triphos})RhH(\mu\text{-}Cl)_2HRh(\text{triphos})](BPh_4)_2$ (**6**) can be prepared either by protonation of (triphos)$RhCl(C_2H_4)$ followed by $NaBPh_4$ addition or by H/Cl exchange between **2** and CH_2Cl_2. Interestingly, **6** exists in solution as a 1:1 mixture of two geometric isomers. The electrochemical behavior of the tetrahydride derivatives in nonaqueous solvents shows that they can reversibly undergo one-electron-redox changes with no change of the primary geometry. By contrast, **6** is unable to reversibly accept or lose electrons. Electrochemical techniques have been used to generate the paramagnetic $[(\text{triphos})RhH(\mu\text{-}H)_2HRh(\text{triphos})]^+$ derivative, which is not directly obtainable by chemical methods. All of the compounds have been fully characterized by IR, NMR, and ESR techniques. Both the mononuclear trihydride **1** and the dimeric tetrahydride **2** are able to straightforwardly transfer hydrogen atoms to unsaturated substrates such as 3,3-dimethylbut-1-ene, dimethyl maleate (DMMA), or dimethyl acetylenedicarboxylate (DMAD). The effectiveness of **2** and **6** to catalytically hydrogenate DMAD and DMMA is investigated and compared to that shown by the mononuclear species $[(\text{triphos})Rh(\pi\text{-DMAD})]BPh_4$ and $[(\text{triphos})Rh(\pi\text{-DMMA})]BPh_4$ as well as a family of homo- and heterobimetallic (μ-H)$_3$ complexes of formula $[(\text{triphos})Rh(\mu\text{-}H)_3M(\text{triphos})]^{n+}$ (M = Rh, Co; *n* = 3, 2). All of the compounds prove active catalysts or catalyst precursors for hydrogenation reactions of DMAD and DMMA. The catalyzed alkyne hydrogenation yields largely the olefin. In the catalytic cycles some of the binuclear compounds are resistant to fragmentation and are responsible for the catalysis.

Introduction

Polynuclear polyhydrides[4] are of interest because of their effective role in homogeneous catalytic hydrogenations and their ability to model surface chemistry.[5] A perusal of the large body of experimental information on polynuclear polyhydrides reveals the paucity of electrochemical data on these compounds[6] as well

---

(1) CNR.

(2) Università di Siena.

(3) Universidad de Valencia.

(4) (a) Moore, D. R.; Robinson, S. D. *Chem. Soc. Rev.* **1983**, *12*, 415. (b) Hlatky, G. G.; Crabtree, R. H. *Coord. Chem. Rev.* **1985**, *65*, 1. (c) Soloveichik, G. L.; Bulydev, B. M. *Russ. Chem. Rev.* **1982**, *51*, 286. (d) Bau, R.; Carroll, W. E.; Hart, D. W.; Teller, R. G.; Koetzle, T. F. In *Transition Metal Hydrides*; Bau, R., Ed.; Advances in Chemistry 167;, American Chemical Society: Washington, DC, 1978; p 73.

(5) (a) Parshall, G. W. *Homogeneous Catalysis*; Wiley-Interscience: New York, 1980. (b) James, B. R. *Homogeneous Hydrogenation*; Wiley-Interscience: New York, 1973. (c) Maitlis, P. M. *Acc. Chem. Res.* **1978**, *11*, 301. (d) Sivak, A. J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1979**, *101*, 4878. (e) Crabtree, R. H; Felkin, H.; Morris, G. E. *J. Organomet. Chem.* **1977**, *141*, 205. (f) Burch, R. R.; Muetterties, E. L.; Day, V. W. *Organometallics* **1982**, *1*, 186. (g) Chaudret, B.; Devillers, J.; Poilblanc, R. *Ibid.* **1985**, *4*, 1727. (h) Wang, H.-H.; Casalnuovo, A. L.; Johnson, B. J.; Mueting, A. M.; Pignolet, L. H. *Inorg. Chem.* **1988**, *27*, 325.

0020-1669/88/1327-4429$01.50/0