2520 *Inorg. Chem.* **1998,** *37,* 2520−2524

Hydride and Gold(triphenylphosphine) Derivatives of Hexarhenium Carbido Octadecacarbonyl

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Received May 15, 1997

Treatment of $[NEt_4]_3[HRe_6C(CO)_{18}]$ in acetone with $Au(PPh_3)Cl$ (1 equiv) provides the gold-capped cluster $[NEt_4]_2[HRe_6C(CO)_{18}(AuPPh_3)]$ (**1**) (82%). Compound **1** crystallizes in the monoclinic space group $P2_1/c$ with $a = 16.519(4)$ Å, $b = 17.849(5)$ Å, $c = 21.540(5)$ Å, $\beta = 99.870(7)°$, and $Z = 4$. The X-ray structure solution shows the cluster anion consists of an octahedral core of rhenium atoms centered on an interstitial carbide with one face capped by a triphenylphosphinegold moiety. Carbonyl ligand positions imply that the hydride ligand is bridging an edge of the Re_3 face trans to the gold cap. Support for this structure is provided by the solution ^{13}C NMR spectrum of **1** recorded at low temperature. The reaction of $Au(PPh_3)Cl$ (2 equiv) with either $[NEt_4]_3[HRe_6C(CO)_{18}]$ or $[NEt_4]_2[H_2Re_6C(CO)_{18}]$ in acetone in the presence of the strong base DBU provides the digold cluster $[NEt_4]_2[Re_6C(CO)_{18}(AuPPh_3)_2]$ (**2**) (85%). The X-ray crystal structure of **2** as an acetone solvate (monoclinic, $P2_1/a$, $a = 19.956(4)$ Å, $b = 21.822(5)$ Å, $c = 18.578(5)$ Å, $\beta = 98.99(1)°$, $Z = 4$) shows a $Re_6(\mu_6\text{-}C)$ octahedral core with trans (1,4) faces capped by the triphenylphosphinegold moieties. Treatment of $[NEt_4]_3[HRe_6C(CO)_{18}]$ in acetone with the more electrophilic reagent $AuPPh_3(NO_3)$ yields $[NEt_4][HRe_6C(CO)_{18}(AuPPh_3)_2]$ (**3**) (52%). The low-temperature ^{13}C NMR spectrum of **3** suggests a 1,4-dicapped structure with a hydride ligand bridging an edge linking the two gold-capped faces. Compound **3** is slowly deprotonated by triethylamine to give **2**.

Introduction

A variety of interesting cluster compounds results formally from the interaction of the octahedral $[Re_6(\mu_6\text{-}C)(CO)_{18}]^{4-}$ cluster core with one or more electrophilic moieties.[1−16] The set for one added electrophile ($X^+ = H^+$, $Re(CO)_3^+$, $M(CO)_n^{2+}$, $Re(CO)_3L^{3+}$) includes the clusters $[HRe_6C(CO)_{18}]^{3-}$,[1] $[Re_7C(CO)_{21}]^{3-}$,[2] $[Re_6C(CO)_{18}M(CO)_n]^{2-}$ ($M = Ru$, $n = 3$; $M = Mo$, $n = 4$),[3] and $[Re_7C(CO)_{21}P(OPh)_3]^{1-}$.[4] The set for two addends (X^+, $Y^+ = H^+$, H^+; H^+, $Re(CO)_3^+$; $Re(CO)_3^+$, $Re(CO)_3^+$; $Re(CO)_3^+$, ML_n^+) is represented by $[H_2Re_6C(CO)_{18}]^{2-}$,[5] $[HRe_7C(CO)_{21}]^{2-}$,[6,7] $[Re_8C(CO)_{24}]^{2-}$,[8] and $[Re_7C(CO)_{21}ML_n]^{2-}$ (M = Rh,[9,10] Ir,[9,11] Pd,[9,12] Pt,[9] Cu,[13] Ag,[13] Au,[6,13] Hg,[14] Tl[15]), and the only previously reported example of three added electrophiles (X^+, Y^+, $Z^+ = H^+$, H^+, $Re(CO)_3^+$) is $[H_2Re_7C(CO)_{21}]^{1-}$.[16]

Of interest are the specific structures adopted by these derivatives both in the solid state and in solution. In all reported cases of metal fragment electrophiles, the addend caps a triangular face of the Re_6C octahedron. However, the hydride ligands have been identified as edge bridging in $[HRe_7C(CO)_{21}]^{2-}$ (two solid-state isomers)[7] and in $[H_2Re_7C(CO)_{21}]^{1-}$.[16] Furthermore, the protonated derivatives show evidence also for facile interconversion of isomeric structures in solution.[6,7,16]

The convenient one-pot syntheses of $[NEt_4]_3[HRe_6(CO)_{18}]$[1] and $[Et_4N]_2[H_2Re_6C(CO)_{18}]$[1] directly from $Re_2(CO)_{10}$ gives us an excellent opportunity to explore the reactivity of these hexanuclear hydride clusters toward electrophiles. In this paper we discuss further examples of two addends, viz., $\{X^+, Y^+\} = \{H^+, AuL^+\}$ and $\{AuL^+, AuL^+\}$, as well as a new compound with three addends, where $\{X^+, Y^+, Z^+\} = \{H^+, AuL^+, AuL^+\}$. The synthetic transformations are summarized in the Scheme.

Experimental Section

General Procedures. All operations were carried out under a nitrogen atmosphere by using standard techniques. Acetone was distilled from potassium carbonate; dichloromethane and methanol were distilled from calcium hydride. Triethylamine (Fisher), 1,8-Diazabicyclo-

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(1) Henly, T. J.; Wilson, S. R.; Shapley, J. R. *Organometallics* **1987**, *6*, 2618.

(2) Ciani, G.; D'Alfonso, G.; Freni, M.; Romiti, P.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1982**, 339.

(3) Hsu, G.; Wilson, S. R.; Shapley, J. R. *Inorg. Chem.* **1996**, *35*, 923.

(4) Simerly, S. W.; Wilson, S. R.; Shapley, J. R. *Inorg. Chem.* **1992**, *31*, 5146.

(5) Ciani, G.; D'Alfonso, G.; Romiti, P.; Sironi, A.; Freni, M. *J. Organomet. Chem.* **1983**, *244*, C27.

(6) Henly, T. J.; Shapley, J. R.; Rheingold, A. L. *J. Organomet. Chem.* **1986**, *310*, 55.

(7) Beringhelli, T.; D'Alfonso, G.; Ciani, G.; Sironi, A. D.; Molinari, H. *J. Chem. Soc., Dalton Trans.* **1988**, 1281.

(8) Ciani, G.; D'Alfonso, G.; Freni, M.; Romiti, P.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1982**, 705.

(9) Henly, T. J.; Shapley, J. R.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1988**, *7*, 441.

(10) (a) Simerly, S. W.; Shapley, J. R. *Inorg. Chem.* **1990**, *29*, 3634. (b) Ralph, S. F.; Simerly, S. W.; Shapley, J. R. *Inorg. Chim. Acta* **1995**, *240*, 615.

(11) (a) Ma, L.; Wilson, S. R.; Shapley, J. R. *Inorg. Chem.* **1990**, *29*, 5133. (b) Ma, L.; Szajek, L. P.; Shapley, J. R. *Organometallics* **1991**, *10*, 1662. (c) Ma, L.; Shapley, J. R. *Inorg. Chim. Acta* **1993**, *212*, 303. (d) Ma, L.; Wilson, S. R.; Shapley, J. R. *J. Am. Chem. Soc.* **1994**, *116*, 787.

(12) Henly, T. J.; Wilson, S. R.; Shapley, J. R. *Inorg. Chem.* **1988**, *27*, 2551.

(13) Beringhelli, T.; D'Alfonso, G.; Freni, M.; Ciani, G.; Sironi, A. *J. Organomet. Chem.* **1985**, *295*, C7.

(14) (a) Henly, T. J.; Shapley, J. R. *Organometallics* **1989**, *8*, 2729. (b) Brand, U.; Coffer, J. L.; Henly, T. J.; Wilson, S. R.; Shapley, J. R. *Inorg. Chem.* **1997**, *36*, 3386.

(15) Brand, U.; Shapley, J. R. *Inorg. Chem.* **1997**, *36*, 253.

(16) Beringhelli, T.; D'Alfonso, G.; Ciani, G.; Sironi, A.; Molinari, H. *J. Chem. Soc., Dalton Trans.* **1990**, 1901.

(17) Hayward, C.-M. T.; Shapley, J. R. *Organometallics* **1988**, *7*, 448.

S0020-1669(97)00575-2 CCC: $15.00

[5.4.0]undec-7-ene (DBU, Aldrich), $[NEt_4][Cl]$ (Aldrich), and $Au(PPh_3)Cl$ (Aldrich) were used as received. $Au(PPh_3)(NO_3)$ was prepared by treating $Au(PPh_3)Cl$ with $AgNO_3$. The salts of $[HRe_6C(CO)_{18}]^{3-}$ and $[H_2Re_6C(CO)_{18}]^{2-}$ were prepared as previously described.[1,17] Enriched $[NEt_4]_3[HRe_6{}^{13}C(^{13}CO)_{18}]$ (ca. 50% ^{13}C) was prepared in the same manner by using $Re_2(^{13}CO)_{10}$ (ca. 50%). Infrared (IR) spectra were recorded on a Perkin-Elmer 1750 FT-IR spectrometer. Elemental analyses were determined in the Microanalytical Laboratory of the School of Chemical Sciences. Fast atom bombardment (FAB) mass spectra (negative ion) were obtained in the School of Chemical Sciences Mass Spectrometry Laboratory; the matrix used was "Magic Bullet" (dithioerythritol−dithiothreitol). ^1H NMR spectra were recorded on a General Electric QE300 spectrometer at 300.1 MHz. ^{31}P NMR spectra were recorded on a GE GN300 spectrometer at 121.5 MHz and referenced to external H_3PO_4. ^{13}C NMR spectra were recorded on a GE GN300 spectrometer at 75.5 MHz or on a GN500 spectrometer at 125.8 MHz. ^1H and ^{13}C NMR spectra were recorded in acetone-d_6 and utilize as references the residual methyl protons at δ 2.04 and the carbonyl resonance at δ 206.0, respectively.

$[NEt_4]_2[HRe_6C(CO)_{18}AuPPh_3]$. $Au(PPh_3)Cl$ (25 mg, 0.050 mmol) and $[NEt_4]_3[HRe_6C(CO)_{18}]$ (101 mg, 0.050 mmol) were stirred in acetone (5 mL) for 3 h. The solution was evaporated to half-volume and then layered with methanol (5 mL). Dark red crystals formed over a period of 2 days. The first crop of crystals was washed with methanol and dried in vacuo. A second crop of crystals was isolated by evaporating the supernatant solution to dryness and recrystallizing the residue from acetone/methanol. Overall yield: 97 mg, 0.041 mmol, 82%. Anal. Calcd for $C_{53}H_{56}N_2O_{18}PRe_6Au$: C, 27.04; H, 2.40; N, 1.19; P, 1.32. Found: C, 27.11; H, 2.36; N, 1.15; P, 1.29. IR (acetone): ν_{CO}, 2034 (w), 1979 (vs), 1968 (s), 1900(w) cm^{-1}. ^1H NMR (acetone-d_6, 20 °C): δ 7.8−7.4 (m, 15H, C_6H_5), 3.48 (q, 16H, $^3J_{H-H}$ = 7.3 Hz, NCH_2 CH_3), 1.38 (tt, 24H, J_{H-H} = 7.3 Hz, J_{N-H} = 1.7 Hz, NCH_2CH_3), −20.76 (s, 1H). $^{13}C\{^1H\}$ NMR (acetone-d_6/ether, −100 °C): δ 420.8 (s, 1C, μ_6-C), 201.1 (s, 3C), 198.9 (s, 2C), 198.2 (s, 4C), 196.5 (s, 2C), 193.0 (s, 2C), 191.8 (s, 2C), 187.2 (s, 1C), 184.5 (s, 2C). $^{31}P\{^1H\}$ NMR (acetone-d_6, 20 °C): δ 75.5 (s). FAB-MS (^{187}Re, ^{197}Au): m/z 2098 $[HRe_6C(CO)_{18}Au(PPh_3)]^-$.

$[NEt_4][HRe_6C(CO)_{18}(AuPPh_3)_2]$. $Au(PPh_3)(NO_3)$ (31 mg, 0.060 mmol) and $[NEt_4]_3[HRe_6C(CO)_{18}]$ (58 mg, 0.029 mmol) were stirred in acetone (5 mL) for 3 h. The dark red solution was evaporated to dryness under vacuum. The residue was extracted with acetone until the extract was colorless. The solution was reduced in volume by evaporation to incipient crystallization and was then layered with methanol (ca. 5 mL). The black microcrystals that formed after 2 days were washed with methanol and dried in vacuo (41 mg, 0.015 mmol, 52%). Anal. Calcd for $C_{63}H_{51}Au_2NO_{18}P_2Re_6$: C, 28.20; H, 1.92; N, 0.52; P, 2.31. Found: C, 28.67; H, 2.11; N, 0.61; P, 2.21. IR (acetone): ν_{CO}, 2046 (w), 1997 (vs), 1983 (m), 1937 (w), 1922 (w) cm^{-1}. ^1H NMR (acetone-d_6, 20 °C): δ 8.4−7.4 (m, 30H, C_6H_5), 3.50 (q, 8H, $^3J_{H-H}$ = 7.3 Hz, NCH_2 CH_3), 1.39 (tt, 12 H, J_{H-H} = 7.3 Hz, J_{N-H} = 1.8 Hz, NCH_2CH_3), −22.55 (s, 1H). $^{13}C\{^1H\}$ NMR (acetone-d_6, −80 °C): δ 430.4 (s, 1C, μ_6-C), 195.3 (s, 2C), 193.8 (s, 6C), 192.2 (s, 2C), 190.4 (s, 2C), 187.5 (s, 2C), 185.7 (s, 2C), 184.6 (s, 2C). $^{31}P\{^1H\}$ NMR (acetone-d_6, 20 °C): δ 77.3 (s). FAB-MS FAB (^{187}Re, ^{197}Au): m/z 2558 $[H_2Re_6C(CO)_{18}(AuPPh_3)_2]^-$.

$[NEt_4]_2[Re_6C(CO)_{18}(AuPPh_3)_2]$. Method 1. From $[Et_4N]_2[H_2Re_6C(CO)_{18}]$. $[Et_4N]_2[H_2Re_6C(CO)_{18}]$ (22 mg, 0.011 mmol) and $Au(PPh_3)Cl$ (13 mg, 0.026 mmol) were dissolved in acetone (40 mL). 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (0.2 mL) was added to the orange solution, and the course of the reaction was monitored periodically by IR spectroscopy. After 24 h, only the characteristic IR bands for $[Re_6C(CO)_{18}(AuPPh_3)_2]^{2-}$ (1968 vs, 1952 m) and $[HRe_6C(CO)_{18}(AuPPh_3)]^{2-}$ (2034 m, 1979 vs) were observed. Another portion of $Au(PPh_3)Cl$ (6 mg) was added, and after another 36 h the reaction appeared complete. Solid $[Et_4N][Cl]$ (100 mg) was added to the solution, which was then filtered, concentrated, and layered with methanol. After 3 days, black crystals of $[Et_4N]_2[Re_6C(CO)_{18}(AuPPh_3)_2]$ (29 mg, 0.10 mmol, 89%) were collected and dried in vacuo. Anal. Calcd for $C_{71}H_{70}N_2O_{18}P_2Re_6Au_2$: C, 30.32; H, 2.51; N, 1.00; P, 2.20. Found: C, 30.62; H, 2.73; N, 0.91; P, 1.91. IR (acetone): ν_{CO}, 1992 (m), 1968 (vs), 1951 (m), 1908 (w) cm^{-1}. ^1H NMR (acetone-d_6, 20 °C): δ 7.8−7.4 (m, 15H, C_6H_5), 3.45 (q, 8H, $^3J_{H-H}$ = 7.3 Hz, NCH_2 CH_3), 1.36 (tt, 12H, J_{H-H} = 7.3 Hz, J_{N-H} = 1.9 Hz, NCH_2CH_3). $^{13}C\{^1H\}$ NMR (acetone-d_6, −80 °C): δ 444.1 (s, 1C, μ_6-C), 199.0 (s, 12C), 188.7 (s, 6C). $^{31}P\{^1H\}$ NMR (acetone-d_6, 20 °C): δ 82.0 (s). FAB-MS (^{187}Re, ^{197}Au): m/z 2558 $[H_2(Re_6C(CO)_{18}(AuPPh_3)]^-$.

Table 1. Crystallographic Data for $[NEt_4]_2[HRe_6C(CO)_{18}(AuPPh_3)]$ (**1**) and $[NEt_4]_2[Re_6C(CO)_{18}(AuPPh_3)_2]$ (**2**)

	1	**2**
formula	$C_{53}H_{55}N_2O_{18}PAuRe_6$	$C_{71}H_{70}N_2O_{18}P_2Au_2Re_6\cdot C_3H_6O$
fw	2353.2	2870.5
space group	$P2_1/c$ (No.14), monoclinic	$P2_1/a$ (No.14), monoclinic
temp	26 °C	26 °C
λ	0.710 73 Å (Mo Kα)	0.710 73 Å (Mo Kα)
a	16.519(4) Å	19.956(4) Å
b	17.849(5) Å	21.822(5) Å
c	21.540(5) Å	18.578(4) Å
b	99.870(7)°	98.99(1)°
V	6257 (6) Å^3	7991 (5) Å^3
Z	4	4
ρ_{calcd}	2.498 g cm^{-3}	2.386 g cm^{-3}
μ	141.38 cm^{-1}	129.26 cm^{-1}
transm coeff	0.132−0.046	0.226−0.068
R^a	0.052	0.052
$R_w{}^b$	0.062	0.062

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = k/([\sigma(F_o)]^2 + [pF_o]^2)$ and $p = 0.020$; $k = 1.79$ for **1** and 1.49 for **2**.

Method 2. From $[Et_4N]_3[HRe_6C(CO)_{18}]$. $[Et_4N]_3[HRe_6C(CO)_{18}]$ (172 mg, 0.0848 mmol) and $Au(PPh_3)Cl$ (105 mg, 0.212 mmol) were dissolved in acetone (125 mL). DBU (1 mL) was added, and the solution was stirred for 3 days until the reaction was complete. Solid $[Et_4N][Cl]$ (100 mg) was added, and the solution was filtered, concentrated, and layered with methanol. The crystals (202 mg, 0.072 mmol, 85%) that formed were washed with methanol, then ether, and finally dried in vacuo.

Method 3. Deprotonation of $[NEt_4][HRe_6C(CO)_{18}(AuPPh_3)_2]$ with Triethylamine. $[NEt_4][HRe_6C(CO)_{18}(AuPPh_3)_2]$ (51 mg, 0.019 mmol) and triethylamine (200 mL) were stirred in acetone (5 mL) for 10 days. The turbid yellow suspension was evaporated to dryness and dried in vacuo. The residue was suspended in acetone (5 mL) with $[Et_4N][Cl]$ (24 mg), and the mixture was stirred for 10 min, then filtered, and the filtrate was evaporated to dryness. The residue was extracted with acetone until the extract was colorless. The acetone solution was evaporated to the point of incipient crystallization, and then was layered with methanol. After 2 days, the first crop of crystals was isolated, washed with methanol, and dried in vacuo. The second crop was obtained by evaporating the supernatant solution and recrystallizing the residue from acetone/methanol. Overall yield: 44 mg, 0.016 mmol, 84%.

X-ray Crystallographic Studies of 1 and 2. For both compounds the X-ray diffraction data were collected on a Syntex $P2_1$ four-circle diffractometer. Brief details are presented in Table 1; a complete description is given in the Supporting Information.

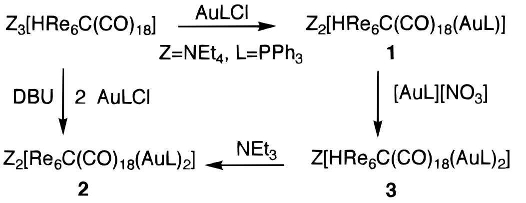
The red, opaque, prismatic crystal of **1** used for data collection had some well-developed faces; however, several faces and edges were damaged. There was no change in the appearance of the sample during the data collection. The dark, opaque, prismatic crystal of **2** used for data collection had well-developed faces. Crystal decay was less than 8%, and there was no change in the appearance of the sample during the data collection.

The structures of both **1** and **2** were solved by direct methods (SHELXS-86); correct positions for the metal atoms were deduced from E-maps. The remaining non-hydrogen atoms were located by least squares-difference Fourier calculations (SHELX-76). In the final cycle of least-squares analysis, anisotropic thermal coefficients were refined for the gold, rhenium, and phosphorus atoms; group isotropic thermal parameters were varied for the disordered tetraethylammonium ions and the hydrogen atoms; and independent isotropic thermal coefficients were refined for the remaining nonhydrogen atoms. The tetraethyl-

Table 2. Metal−Metal, Metal−μ_6-Carbon, and Gold−Phosphorus Distances (Å) for the Clusters in Compounds **1** and **2**

	$[HRe_6C(CO)_{18}(AuPPh_3)]^{2-}$	$[Re_6C(CO)_{18}(AuPPh_3)_2]^{2-}$
Au1−Re1	2.851(2)	2.849(2)
Au1−Re2	2.975(2)	2.863(2)
Au1−Re3	2.795(2)	2.915(2)
Au2−Re4		2.878(2)
Au2−Re5		2.873(2)
Au2−Re6		2.898(2)
Re1−Re2	3.098(2)	3.060(2)
Re1−Re3	3.017(2)	3.056(2)
Re2−Re3	2.997(2)	3.078(2)
Re1−Re5	3.016(2)	2.993(2)
Re1−Re6	2.967(2)	3.014(2)
Re2−Re4	3.044(2)	2.994(2)
Re2−Re6	2.987(2)	2.986(2)
Re3−Re4	3.038(2)	2.995(2)
Re3−Re5	2.993(2)	3.013(2)
Re4−Re5	3.004(2)	3.070(2)
Re4−Re6	3.071(2)	3.082(2)
Re5−Re6	3.057(2)	3.038(2)
Re1−C	2.17(3)	2.07(2)
Re2−C	2.12(3)	2.16(4)
Re3−C	2.14(3)	2.12(3)
Re4−C	2.15(3)	2.23(3)
Re5−C	2.16(3)	2.12(4)
Re6−C	2.09(3)	2.17(3)
Au1−P1	2.271(9)	2.30(1)
Au2−P2		2.32(1)

Scheme 1



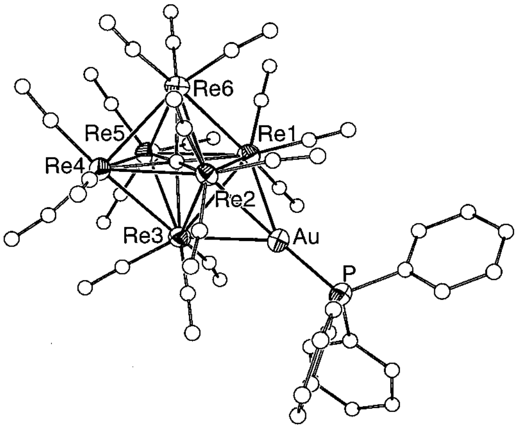


Figure 1. ORTEP diagram of the cluster $[HRe_6C(CO)_{18}AuPPh_3]^{2-}$ in compound **1**.

ammonium ions were refined as ideal rigid groups. Successful convergence of the solutions was indicated by the maximum shift/error for the final cycle. The highest peak in the final difference Fourier maps was in the vicinity of the disordered cations. Selected distances for the cluster cores are displayed in Table 2; selected angles are presented in Table 3.

Results and Discussion

Synthesis and Interconversion of Compounds 1−3 (Scheme 1). Treatment of $[NEt_4]_3[HRe_6C(CO)_{18}]$ in acetone with 1 equiv of $Au(PPh_3)Cl$ causes rapid formation of the monogold derivative $[NEt_4]_2[HRe_6C(CO)_{18}(AuPPh_3)]$ (**1**), which is isolated in 82% yield as dark red crystals. A stoichiometric quantity of $Au(PPh_3)Cl$ must be used, or a mixture of **1** and the hydrido digold complex $[NEt_4][HRe_6C(CO)_{18}(AuPPh_3)_2]$ (**3**) forms. Even when the product **1** is obtained by careful recrystallization, appearing pure by elemental analysis and mass spectroscopy, it may be contaminated with small quantites of **3**, as determined by NMR spectroscopy. Pure samples of **3**, as a black microcrystalline powder, are obtained by the reaction of $[NEt_4]_3$-$[HRe_6C(CO)_{18}]$ with 2 equiv of the more electrophilic gold reagent $Au(PPh_3)(NO_3)$. Complex **3** is slowly deprotonated by an excess of triethylamine in acetone, and the complex $[NEt_4]_2$-$[Re_6(CO)_{18}(AuPPh_3)_2]$ (**2**) is isolated as dark crystals in 82% yield. Compound **2** is obtained more directly by treating either $[NEt_4]_3[HRe_6C(CO)_{18}]$ or the somewhat more available precursor $[NEt_4]_2[H_2Re_6C(CO)_{18}]^{17}$ with a slight excess of $Au(PPh_3)$-Cl in the presence of the strong base DBU. Monitoring the IR spectrum during these reactions shows that **1** appears as an intermediate. Evidently DBU is effective in deprotonating **1** in order to allow further reaction with $Au(PPh_3)Cl$ to form **2**.

The negative ion FAB mass spectra obtained for **1** show the ion multiplet corresponding to the molecular cluster together with weaker fragment ions. Interestingly, the mass spectra for both **2** and **3** show a cluster ion with isotope distributions corresponding closely to the formula $[H_2Re_6C(CO)_{18}(AuPPh_3)_2]^-$, indicating protonation by the matrix. A figure comparing the observed and calculated isotope distribution is included in the Supporting Information.

Crystal Structure of $[NEt_4]_2[HRe_6C(CO)_{18}AuPPh_3]$ (1). In the crystal structure of the monogold complex **1**, the molecular cluster anion consists of an octahedron of rhenium atoms containing an interstitial carbide and capped on one face by a triphenylphosphinegold group (see Figure 1). A survey of the metal−metal bond distances (Table 2) reveals that there is a pattern to the variation of the Au−Re and Re−Re bond lengths in the cluster framework. The Au−Re3 bond is shorter than the remaining two Au−Re distances, and on the capped face the vector Re1−Re2, which is opposite Re3, is the longest. The bond distances Re1−Re6 and Re2−Re6 are short (Re6 is the atom opposite Re3 in the octahedron), as is Re3−Re5. On the

Table 3. Selected Bond Angles (deg) for the Clusters in Compounds **1** and **2**

		$[HRe_6C(CO)_{18}AuPPh_3]^{2-}$			
Re1−Au−P	150.0(2)	Re2−Au−P	133.0(2)	Re3−Au−P	141.9(2)
Re1−Au−Re2	64.21(5)	Re1−Au−Re3	64.60(5)	Re2−Au−Re3	62.50(5)
Au−P−C71	117.4(8)	Au−P−C81	113.3(8)	Au−P−C91	114.4(8)
		$[Re_6C(CO)_{18}(AuPPh_3)_2]^{2-}$			
Re1−Au1−P1	148.1(3)	Re2−Au1−P1	142.0(3)	Re3−Au1−P1	134.7(3)
Re4−Au2−P2	138.7(3)	Re5−Au2−P2	143.1(3)	Re6−Au2−P2	144.5(2)
Re1−Au1−Re	264.78(6)	Re1−Au1−Re3	64.03(6)	Re2−Au1−Re3	64.36(5)
Re4−Au2−Re5	64.54(6)	Re4−Au2−Re6	64.50(6)	Re5−Au2−Re6	63.53(5)
Au1−P1−C71	110.0(9)	Au1−P1−C81	116(1)	Au1−P1−C91	114.7(8)
Au2−P2−C101	114.4(8)	Au2−P2−C111	112.7(10)	Au2−P2−C121	112.7(9)

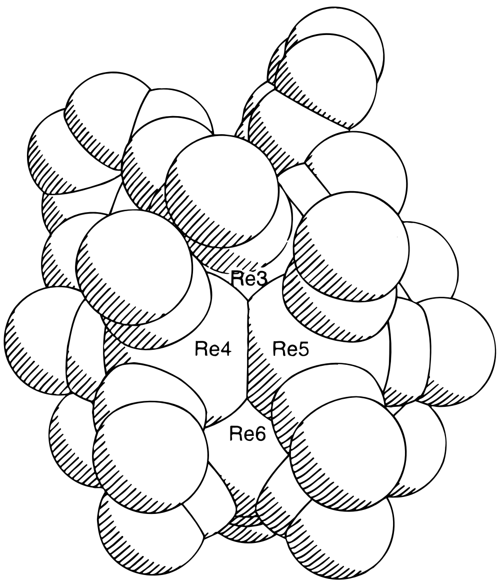


Figure 2. ChemDraw space-filling diagram of the structure of $[HRe_6C(CO)_{18}AuPPh_3]^{2-}$ based on the crystallographic coordinates. The view is from above the Re4−Re5 bond and shows the opening due to the proposed location of the hydride ligand bridging this bond.

face opposite the cap, the bond Re4−Re5, which is adjacent to Re3, is the shortest in this face. These variations suggest that the Re_6 core is internally compensating for the distortion induced by the presence of the gold cap.

The position of the hydride ligand may be deduced by inspection of Re−Re−C(O) bond angles. In all sets of these angles Re_x-Re_y-C_{yi}, one carbonyl on Re_y subtends an angle significantly less than 100° with respect to the Re_x-Re_y bond, with the exception of the sets Re4−Re5−C5i and Re5−Re4−C4i (see bond angle table in Supporting Information). Thus, there is a specific ′hole′ in the carbonyl ligand shell positioned over the Re4−Re5 bond, and this distortion may be attributed to the hydride ligand bridging this bond. The presence of this opening is also easily seen in a space filling drawing of the structure, as shown in Figure 2. This location for the hydride ligand, on an edge of the octahedral face opposite that of the capped face, is the same as that found in one isomer of $[HRe_7C(CO)_{21}]^{2-}$.[7]

Crystal Structure of $[NEt_4]_2[Re_6C(CO)_{18}(AuPPh_3)_2]$ (2). The molecular structure of the cluster anion in **2** consists of an octahedron centered on an interstitial carbon atom and capped on opposite faces of the octahedron by triphenylphosphinegold groups (see Figure 3). Table 2 lists metal−metal and metal-carbide distances and Table 3 provides selected angles for this structure. In general the structural is highly regular, with smaller variations in both Re−Au and Re−Re distances than in the case of the monogold cluster in **1**.

The characterization of $[Re_6C(CO)_{18}(AuPPh_3)_2]^{2-}$ completes a set of related complexes that began with $[Re_8C(CO)_{24}]^{2-}$ [8] and was extended with $[Re_7C(CO)_{21}(AuPPh_3)]^{2-}$.[6,13] Each of these clusters has a 1,4 (trans) disposition of the two face-capping groups. Analogous 1,4 face-capped structures have been observed for the osmium−gold compound $Os_6(CO)_{18}(AuPMe_3)_2$[18] as well as for the related copper complexes $Os_6(CO)_{18}(CuNCMe)_2$[18] and $Ru_6(CO)_{18}(CuC_6H_5Me)_2$.[19] However, contrasting structures are displayed by other $M_6(AuL)_2$ compounds, viz., $Ru_6C(CO)_{16}(AuL)_2$ (L = $PMePh_2$,[20] PPh_3[21]), in which the gold moieties are in trans disposition but edge bridging, and $Rh_6(CO)_{13}(AuPPh_3)_2$, in which the gold units cap adjacent faces (1,2) and develop an Au−Au bond.[22] It is clear that the number of carbonyl ligands on the M_6 cluster core has a dominant effect on the placement of the two metal fragment addends.

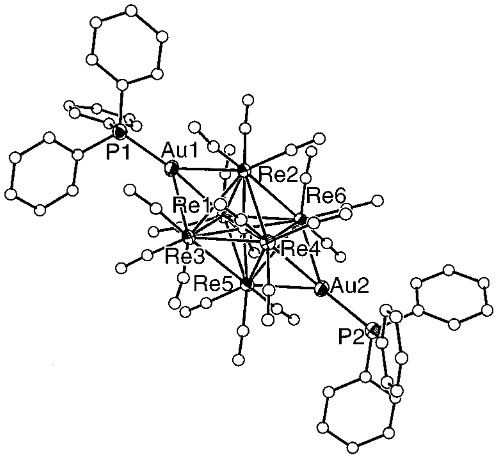


Figure 3. ORTEP diagram of the cluster $[Re_6C(CO)_{18}(AuPPh_3)_2]^{2-}$ in compound **2**.

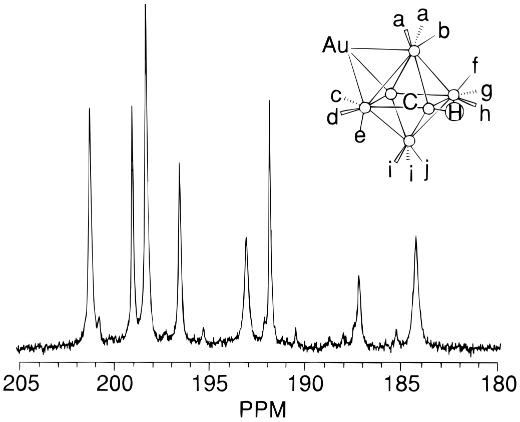


Figure 4. Carbonyl region $^{13}C\{^1H\}$ NMR spectrum of **1** at −100 °C.

Solution Structures and Dynamics of Clusters in 1−3. The ^{13}C NMR spectrum of the ^{13}CO-enriched cluster $[NEt_4]_2[HRe_6C(CO)_{18}AuPPh_3]$ (**1**) at 125.8 MHz and in a mixed solvent system (acetone-d_6/diethyl ether) shows a relatively sharp spectrum at −100 °C (Figure 4). Three peaks at δ 184.5, 187.2, and 193.0 are somewhat broader, which we ascribe to slow exchange at this temperature. There are also very minor resonances, some of which overlap with resonances of **1**, arising from contamination of the sample by the digold complex **3**. When one takes the presence of **3** into account, the eight signals observed for the cluster **1** are in the approximate ratios of 3:2:4:2:2:2:1:2 from low to high field. Although no specific assignments can be established, the overall spectrum is consistent with the X-ray crystal structure of **1**, that is, a structure in which a hydride ligand is bridging two rhenium atoms on the face opposite the gold cap. For this structure one would predict

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(18) Diebold, M. P.; Johnson, B. F. G.; Lewis, J.; McPartlin, M.; Powell, H. R. *Polyhedron* **1990**, *9*, 75.

(19) Ansell, C. B.; Modrick, M. A.; Bradley, J. S. *Acta Crystallogr.* **1984**, *C40*, 365.

(20) Bunkhill, S. R.; Holden, H. D.; Johnson, B. F. G.; Lewis, J.; Pain, G. N.; Raithby, P. R.; Taylor, M. J. *J. Chem. Soc., Chem. Commun.* **1984**, 25.

(21) Bruce, M. I.; Horn, E.; Humphrey, P. A.; Tiekink, E. R. T. *J. Organomet. Chem.* **1996**, *518*, 121.

(22) Fumagalli, A.; Martinengo, S.; Albano, V. G.; Braga, D.; Grepioni, F. *J. Chem. Soc., Dalton Trans.* **1989**, 2343.

a total of 10 resonances: eight 2C and two 1C signals. Only eight signals are actually observed, and the relative intensities suggest some overlap of resonances. Nevertheless, structures with symmetries different from C_s are not supported.

On warming the sample of **1**, generalized peak broadening occurs in the spectrum, and total coalescence to one broad peak is observed by ca. −50 °C. On the basis of previous experience with these clusters, we expect that localized exchange within each $Re(CO)_3$ group occurs rather than internuclear carbonyl movement. However, complete equilibration of all carbonyls (in the absence of accidental overlap) would require migration of the triphenylphosphinegold group as well as the hydride ligand over the faces of the cluster. Migration of the hydride ligand is well established for $[HRe_7C(CO)_{21}]^{2-}$,[6,7] but gold migration was not seen in $[Re_7C(CO)_{21}AuPPh_3]^{2-}$.[6,13] On the other hand, migration of gold moieties has been postulated to explain similar NMR results for both $Ru_6C(CO)_{16}(AuPEt_3)_2$[20] and $Rh_6(CO)_{13}(AuPPh_3)_2$.[22]

The ^{13}C NMR spectrum (not shown) of the digold complex $[NEt_4]_2[Re_6(CO)_{18}(AuPPh_3)_2]$ (**2**) at −80 °C shows two resonances, slightly broadened, at δ 188.7 and 199.0 in the intensity ratio of 1:2. We ascribe the presence of two signals to the two sets of carbonyl ligands shown in the solid-state structure (see Figure 3), i.e., the six carbonyls pointing toward the middle faces of the cluster and the twelve carbonyls pointing away. Warming the sample results in broadened resonances with coalescence at −50 °C, and further warming to 20 °C results in a single sharp signal. In this case there is no need to consider migration of the gold moieties, since the observed equilibration can be accomplished simply by localized rotation of the $Re(CO)_3$ groups.

The ^{13}C NMR spectrum at −90 °C of the cluster $[NEt_4][HRe_6(CO)_{18}(AuPPh_3)_2]$ (**3**) shows seven sharp peaks at δ 184.6 (2C), 185.7 (2C), 187.5 (2C), 190.4 (2C), 192.2 (2C), 193.8 (6C), and 195.3 (2C) (Figure 5). The peak at δ 184.6 is coupled to the hydride resonance with J ca. 6 Hz and the peak at δ 190.4 has an unresolvable coupling to the hydride, but the remaining peaks show no significant proton coupling. The only structure with a 1,4 disposition of gold atoms on the Re_6 octahedron that is consistent with the pattern of peaks observed in the low-temperature spectrum is that having the hydride ligand bridging an edge connecting the capped faces (overall C_2 symmetry). The 6C signal may be attributed to the two $Re(CO)_3$ groups furthest removed from the hydride-bridged edge, with the expected chemical shift differences diminished by the distance or by rapid local rotation. All of the signals broaden equally as the sample temperature is raised, with coalescence occurring at approxmately −20 °C, and a somewhat broad singlet at δ 191 is observed at 40 °C. This equilibration of the eighteen carbonyl ligands is likely due to migration of the hydride ligand over the edges of the Re_6 core between the Au caps together with local exchange in the $Re(CO)_3$ groups.

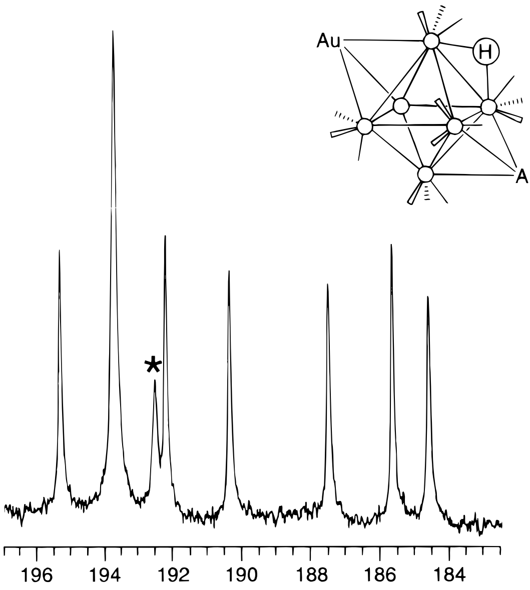

Figure 5. Carbonyl region 75.5 MHz $^{13}C\{^1H\}$ NMR spectrum of **3** at −90 °C. The asterisk indicates an impurity peak.

The only other structural isomer with the required symmetry to explain the limiting ^{13}C NMR spectrum for **3** is a 1,2-digold isomer with the hydride ligand bridging the edge opposite the edge of the octahedron common to both gold atoms. We consider this structure unlikely because the deprotonated complex **2** has gold atoms on opposite faces, and it is not likely that the addition of a proton will have such a strong effect as to suddenly favor 1,2-substitution. Furthermore, the 1,2 structure would require migration of the triphenylphosphinegold moieties in order to achieve complete equilibration of the carbonyls.

Conclusions

We have shown that the complex $[NEt_4]_3[HRe_6C(CO)_{18}]$ reacts readily with triphenylphosphine gold complexes to form the hydrido monogold- and digold-capped clusters **1** and **3**. The hydride ligands in **1** and **3** are believed to be edge-bridging, based on the low-temperature limiting ^{13}C NMR spectra of these complexes. The edge-bridging locations of the hydride ligands is in marked contrast to the face-capping found for the triphenylphosphine gold ligands in **1** and **2**, consistent with previous conclusions by Beringhelli et al.[7] from studies comparing $[Re_7C(CO)_{21}AuPPh_3]^{2-}$ and $[HRe_7C(CO)_{21}]^{2-}$.

Acknowledgment. This work was supported by National Science Foundation Grant No. DMR 89-20538 to the Frederick Seitz Materials Research Laboratory of the University of Illinois.

Supporting Information Available: A figure comparing calculated and observed ion multiplets for **2** and **3** and a complete description of the X-ray crystallographic studies of **1** and **2** including tables of atomic coordinates, bond distances, bond angles, and thermal parameters are available (25 pages). Ordering information is given on any current masthead page.

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