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Mixed-Metal Gold Phosphine Cluster Complexes and Their Reactivity toward Triphenylphosphine

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The reactivity of several mixed-metal gold clusters toward PPh_3 has been investigated. $\{Au_4Re(H)_4[P(p\text{-tol})_3]_2(PPh_3)_4\}BPh_4$ (**1**), $[AuRu(H)_2(dppm)_2(PPh_3)]PF_6$ (**2**), $IrH(CO)(PPh_3)_3$, and $[Ir(H)_2(bpy)(PPh_3)_2]BF_4$ were made by the reaction of PPh_3 with $\{Au_5Re(H)_4[P(p\text{-tol})_3]_2(PPh_3)_5\}^{2+}$, $[Au_2Ru(H)_2(dppm)_2(PPh_3)_2](PF_6)_2$, $[AuIr(H)(CO)(PPh_3)_4]PF_6$, and $[AuIr(H)_2(bpy)(PPh_3)_2(CH_3CN)](BF_4)_2$, respectively. The two new mixed-metal gold compounds $[Au_2Ir(CO)_2(PPh_3)_4]PF_6$ (**3**) and $\{AuRu(H)_2[P(OMe)_3]_4PPh_3\}NO_3$ (**4**), which were made by the reaction of CO with $[Au_2Ir(H)(PPh_3)_4(NO_3)]BF_4$ and $AuPPh_3NO_3$ with $H_2Ru[P(OMe)_3]_4$, respectively, did not readily react with PPh_3. All of these clusters were characterized by ^1H and ^{31}P NMR spectroscopy and by standard analytical methods. Compound **1** was also characterized by single-crystal X-ray diffraction at −95 °C. It was isolated as the BPh_4^- salt and crystallized in the monoclinic space group *P*2/*c* with unit cell parameters $a = 27.72$ (1) Å, $b = 16.591$ (5) Å, $c = 27.73$ (4) Å, $\beta = 99.15$ (6)°, $Z = 4$, and $R = 0.095$. Its structure consisted of an edge-bridged tetrahedron with an average Au–Au bond distance of 2.857 Å and an average Re–Au distance of 2.726 Å. The apparent driving force of the PPh_3 reactions is the formation of $[Au(PPh_3)_2]^+$, which is always observed as a product when $[AuPPh_3]^+$ is extruded.

Introduction

There has been considerable recent interest in the preparation of mixed-metal cluster compounds that contain gold,[1-11] because of their potential use as bimetallic catalysts and as catalyst models.[12,13] The synthetic routes to these discrete cluster compounds have generally included (i) the combination of a carbonylmetalate with $AuPR_3X$, e.g. $[Os_4H_3(CO)_{12}]^- + AuPPh_3Cl \rightarrow [Os_4H_3(CO)_{12}AuPPh_3]$,[14] (ii) the replacement of metal hydrides by $AuPR_3$ units, e.g. $[(NO_3)Ir(PPh_3)_2H(AuPPh_3)_2]^+ + AuPPh_3NO_3 \rightarrow [(NO_3)Ir(PPh_3)_2(AuPPh_3)_3]^+$,[15] and (iii) the formation of new clusters upon the reduction of $AuPPh_3^+$ in the presence of a coordinatively unsaturated metal complex, e.g. $RhH(CO)(PPh_3) + AuPPh_3NO_3 \rightarrow \{RhH(CO)(PPh_3)_2[Au(PPh_3)]_3\}^+$.[3] It is known in gold cluster chemistry that the addition of 1 equiv or more of PPh_3 to a gold cluster can lead to the formation of a new cluster, e.g. $[Au_9(PPh_3)_8]^{3+} + PPh_3 \rightarrow [Au_8(PPh_3)_7]^{2+} + [Au(PPh_3)_2]^+$.[16] We have utilized this method of cluster transformation in the synthesis of some new mixed-metal gold clusters and report here the reactivity of various mixed-metal

Table I. Summary of Crystal Data and Intensity Collection for **1**

Crystal Parameters and Measurement of Intensity Data	
formula	$\{Au_4Re(H)_4[P(p\text{-tol})_3]_2(PPh_3)_4\}(BPh_4)$ (**1**)
cryst syst	monoclinic
space group	*P*2/*c* (No. 13)
cryst dimens, mm³	0.30 × 0.05 × 0.20
T, °C	−95
cell params	
a, Å	27.72 (1)
b, Å	16.591 (5)
c, Å	27.73 (4)
β, deg	99.15 (6)
V, Å³	12590 (29)
Z	4
calcd density, g cm⁻³	1.562
abs coeff, cm⁻¹	58.1
max, min, av trans factors	1.00, 0.74, 0.87
mol formula	$C_{138}H_{132}BP_6Au_4Re$
fw	2961.16
diffractometer	CAD 4
radiation	Mo K$\bar{\alpha}$ ($\lambda = 0.71069$ Å), graphite monochromatized
scan type; range (2*θ*), deg	*ω* scan; 0–43
unique reflcns measd (region)	15058 ($\pm h,+k,+l$)
obsd reflcns[a]	7892 [$F_o^2 \geq \sigma(F_o^2)$]
Refinement by Full-Matrix Least Squares	
no. of params	556
R^b	0.095
$R_w{}^b$	0.113
GOF[b]	2.553
p^a	0.04

[a] The intensity data were processed as described in: *CAD 4 and SDP-PLUS User's Manual*; B. A. Frenz & Associates: College Station, TX, 1982. The net intensity $I = [K/\mathrm{NPI}](C - 2B)$, where $K = 20.1166$ (attenuator factor), NPI = ratio of fastest possible scan rate to scan rate for the measurement, C = total count, and B = total background count. The standard deviation in the net intensity is given by $[\sigma(I)]^2 = (K/\mathrm{NPI})^2[C + 4B + (pI)^2]$, where p is a factor used to downweight intense reflections. The observed structure factor amplitude F_o is given by $F_o = (I/Lp)^{1/2}$, where Lp = Lorentz and polarization factors. The $\sigma(I)$'s were converted to the estimated errors in the relative structure factors $\sigma(F_o)$ by $\sigma(F_o) = {}^1/_2[\sigma(I)/I]F_o$. [b] The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma(F_o)]^2$. The unweighted and weighted residuals are defined as $R = \sum(||F_o| - |F_c||)/\sum|F_o|$ and $R_w = [(\sum w(|F_o| - |F_c|)^2)/(\sum w|F_o|^2)]^{1/2}$. The error in an observation of unit weight (GOF) is $[\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$, where NO and NV are the numbers of observations and variables, respectively.

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(1) 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.

(2) 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.

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

(4) Mingos, D. M. P.; Wardle, R. W. M. *J. Chem. Soc., Dalton Trans.* **1986**, 73. Gilmour, D. I.; Mingos, D. M. P. *J. Organomet. Chem.* **1986**, *302*, 127. Hall, K. P.; Mingos, D. M. P. *Prog. Inorg. Chem.* **1984**, *32*, 237 and references cited therein.

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

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

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

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

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

(10) Braunstein, P.; Rosé, J.; Manotti-Lanfredi, A. M.; Tiripicchio, A.; Sappa, E. *J. Chem. Soc., Dalton Trans.* **1984**, 1843. Braunstein, P.; Rosé, J. *Gold Bull.* **1985**, *18*, 17.

(11) 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.

(12) Sinfelt, J. H. *Bimetallic Catalysts*; Wiley: New York, 1983; Chapters 1 and 2.

(13) Evans, J.; Jingxing, G. *J. Chem. Soc., Chem. Commun.* **1985**, 39.

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

(15) 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.

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Table II. Positional Parameters and Their Estimated Standard Deviations for the Core of $\{Au_4Re(H)_4[P(p\text{-tol})_3]_2(PPh_3)_4\}^{+}$[a]

atom	*x*	*y*	*z*	*B*, Å^2
Au1	0.22530 (6)	0.1999 (1)	−0.01499 (6)	3.65 (4)
Au2	0.20077 (5)	0.0383 (1)	−0.00219 (6)	2.93 (4)
Au3	0.28021 (6)	−0.0791 (1)	0.00812 (6)	3.25 (4)
Au4	0.27306 (6)	0.0312 (1)	0.08448 (6)	3.35 (4)
Re	0.29470 (6)	0.0820 (1)	−0.00368 (6)	2.82 (4)
P1	0.1876 (5)	0.3171 (9)	−0.0214 (5)	5.7 (4)
P2	0.1188 (4)	0.0192 (8)	0.0003 (4)	3.5 (3)
P3	0.2900 (4)	−0.2130 (8)	0.0105 (4)	4.2 (3)
P4	0.2658 (4)	0.0008 (8)	0.1634 (4)	3.9 (3)
P5	0.3623 (4)	0.1500 (8)	0.0433 (4)	3.4 (3)
P6	0.2740 (4)	0.0453 (8)	−0.0890 (4)	3.3 (3)

[a] Phenyl group positional parameters are given in the supplementary material. Anistropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

gold clusters with PPh_3.

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 internal standard trimethyl phosphate (TMP), with positive shifts downfield. Infrared spectra were recorded on a Beckman Model 4250 grating spectrometer. Conductivity measurements were made with use of a Yellow Springs Model 31 conductivity bridge. FABMS experiments were carried out with use of a VG Analytical, Ltd., 7070E-HF high-resolution double-focusing mass spectrometer equipped with a VG 11/250 data system.[1] Microanalyses were carried out by M-H-W Laboratories, Phoenix, AZ. Solvents were dried and distilled prior to use. $[Au_4Ir(H)_2(PPh_3)_6]BF_4$,[17] $[AuIr(H)_2(bpy)(PPh_3)_3](BF_4)_2$,[2] $[Au_2Ru(H)_2(dppm)_2(PPh_3)_2](NO_3)_2$,[2] $[Ir(H)_2(bpy)(PPh_3)_2]BF_4$,[2] $[AuIr(H)(CO)(PPh_3)_4]PF_6$,[2] $[Au_3Rh(H)(CO)(PPh_3)_5]PF_6$,[3] $H_2Ru[P(OMe)_3]_4$,[18] $\{Au_4Re(H)_4[P(p\text{-tol})_3]_2(PPh_3)_4\}PF_6$,[1] $[Au_6Pt(PPh_3)_7](BPh_4)_2$,[1] and $[Au_2Ir(H)(PPh_3)_4(NO_3)]BF_4$[15] (bpy = 2,2′-bipyridine, dppm = bis(diphenylphosphino)methane, *p*-tol = *p*-tolyl) were prepared as described in the literature.

X-ray Structure Determination. Collection and Reduction of X-ray Data. A summary of crystal and intensity data for $\{Au_4Re(H)_4[P(p\text{-tol})_3]_2(PPh_3)_4\}BPh_4$ (**1**) is presented in Table I. A crystal of the compound was coated with a viscous high-molecular-weight hydrocarbon and secured to the end of a glass fiber by cooling to −95 °C. The crystal remained stable at this temperature during data collection. The crystal class and space group were unambiguously determined by the Enraf-Nonius CAD4-SDP-PLUS peak search, centering, and indexing programs,[19] by the presence of systematic absences observed during data collection, and by successful solution and refinement (vide infra). The intensities of three standard reflections were measured every 1.5 h of X-ray exposure time, and no decay was observed. Empirical absorption corrections were applied by use of ψ-scan data and the programs PSI and EAC.[19]

Solution and Refinement of the Structure. The structure was solved by conventional heavy-atom techniques. The metal atoms were located by Patterson syntheses, and full-matrix least-squares refinement and difference Fourier calculations were used to locate all remaining nonhydrogen atoms of the cation. At this point the *R* value was about 10% with only the metal and phosphorus atoms refined anisotropically and location of the atoms of the BPh_4^- counterion was proving difficult. In addition, the B and C phenyl rings were somewhat disordered as evidenced by the large thermal parameters for some of the carbons. The presence of the BPh_4^- counterion was independently verified by analytical and spectroscopic data and by a packing analysis, which showed the presence of a hole of the appropriate size. Difference Fourier analysis of this region revealed spread-out electron density. Numerous attempts were made at refining "peaks" in this region as carbon atoms, but a model for even a single phenyl ring was not obtained. We simply could not succeed in locating more than several of the BPh_4^- atoms. We therefore omitted all atoms in this region from the model and carried out the final refinement of the cation. This proceeded in a satisfactory way. The final difference Fourier map revealed electron density in the region of the totally disordered BPh_4^- counterion, but no further attempts were made to improve the model. The distances and angles within the phenyl rings of the cation (supplementary material) show that the model is reasonable. We are quite confident in the reliability of the structural parameters of the Au_4ReP_6 core, which are unaffected by the disorder in the anion, and of course this is the important part of the structure for our purposes. The atomic scattering factors were taken from the usual tabulation,[20] and the effects of anomalous dispersion were included in F_c by using Cromer and Ibers[21] values of $\Delta f'$ and $\Delta f''$. The final positional and thermal parameters of all refined atoms are given in Table II and as supplementary material. An ORTEP drawing of the cation including the labeling scheme is shown in Figure 1 and as supplementary material. Complete listings of distances, angles, thermal parameters, least-squares planes, and structure factor amplitudes are included as supplementary material.[22]

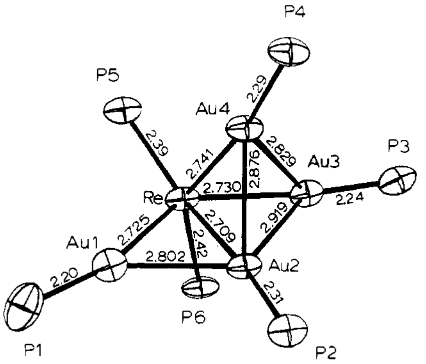

Figure 1. ORTEP drawing (50% probability boundaries) of the coordination core of $\{Au_4Re(H)_4[P(p\text{-tol})_3]_2(PPh_3)_4\}BPh_4$ (**1**) including selected distances (Å). Selected angles (deg) are as follows, where numbers refer to respective Au atoms: 1–Re–2, 62.06 (4); 1–Re–3, 126.97 (5); 1–Re–4, 94.17 (5); 2–Re–3, 64.91 (4); 2–Re–4, 63.70 (4); 3–Re–4, 62.28 (4); 1–2–3, 117.13 (5); 1–2–4, 89.66 (5); 3–2–4, 58.44 (4); 2–3–4, 60.01 (4); 2–4–3, 61.55 (4); Re–1–P1, 163.8 (2); Re–2–P2, 172.3 (2); Re–3–P3, 162.9 (2); Re–4–P4, 170.7 (2); P5–Re–P6, 134.0 (2). Esd's in the last significant figure for M–P and Au–Au distances are 1 and 2, respectively, and for Re–1, Re–2, Re–3, and Re–4 the esd's are 2, 1, 2, and 1, respectively.

Preparation of Compounds. $\{Au_4Re(H)_4[P(p\text{-tol})_3]_2(PPh_3)_4\}BPh_4$ **(1)** was made via a synthesis alternate to that reported in ref 1 as follows: $\{Au_5Re(H)_4[P(p\text{-tol})_3]_2(PPh_3)_5\}(PF_6)_2$[3] (154 mg, 0.046 mmol) and $NaBPh_4$ (35 mg, 0.102 mmol) were dissolved in freshly distilled and degassed THF and allowed to stir overnight. The solvent was removed in vacuo and the residue redissolved in CH_2Cl_2 and filtered through diatomaceous earth. The CH_2Cl_2 was then removed in vacuo and the oily residue redissolved in MeOH and filtered. Upon removal of the MeOH under vacuum a yellow precipitate was obtained. Recrystallization from CH_2Cl_2–pentane produced X-ray-quality crystals in 37% yield. Spectroscopic data for the BPh_4^- salt was identical with that of the PF_6^- salt.[1]

$[AuRu(H)_2(dppm)_2(PPh_3)]PF_6$ **(2).** PPh_3 (14.0 mg, 0.0534 mmol) was dissolved in 3 mL of CH_2Cl_2 and was added to a solution of $[Au_2Ru(H)_2(dppm)_2(PPh_3)_2](PF_6)_2$ (111.3 mg, 0.0535 mmol) in 3 mL of CH_2Cl_2. The colorless solution was stirred for 1 h, at which time 20 mL of Et_2O was added which induced precipitation of a light colored solid. This product was collected, washed with Et_2O, and dried in vacuo. A total of 79.3 mg of this creamy white powder was collected, which consisted of **2** along with the side product $Au(PPh_3)_2PF_6$. Crystals of complex **2** were obtained from a CH_2Cl_2–Et_2O solvent mixture and characterized by X-ray diffraction, which will be reported elsewhere.[23]

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(16) Van der Velden, J. W. A.; Bour, J. J.; Bosman, W. P.; Noordik, J. H. *Inorg. Chem.* **1983**, *22*, 1913.

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

(18) Gerlach, D. H.; Peet, W. G.; Muetterties, E. L. *J. Am. Chem. Soc.* **1972**, *94*, 4545.

(19) All calculations were carried out on PDP 8A and 11/34 computers with the use of the Enraf-Nonius CAD 4-SDP-PLUS programs. This crystallographic computing package is described by: Frenz, B. A. In *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R., van Konigsveld, H., Bassi, G. C., Eds.; Delft University: Delft, Holland, 1978; pp 64–71. Frenz, B. A. In *Structure Determination Package and SDP-PLUS User's Guide*; B. A. Frenz & Associates, Inc.: College Station, TX, 1982.

(20) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2.4. Cromer, D. T. *Ibid.*, Table 2.3.1.

(21) Cromer, D. T.; Ibers, J. A. In ref 20.

(22) See the paragraph at the end of the paper regarding supplementary material.

^{31}P NMR (CH_2Cl_2, 25 °C): δ 45.7 (t, J = 23.8 Hz, int = 1), 3.7 (t of d, J = 36.9 and 23.8 Hz, int = 2), -0.3 (t, J = 36.9 Hz, int = 2). ^{1}H NMR in hydride region (CD_2Cl_2, 25 °C): δ -4.51 (d of d of t, $J_{H-P(A)}$ = 54.03, $J_{H-P(B)}$ = 32.31, $J_{H-P(C)}$ = 12.44 Hz). The equivalent conductance (85.7 cm^2 mho mol^{-1}) is indicative of a 1:1 electrolyte in CH_3CN solution. Anal. Calcd for $AuRuP_6C_{68}H_{61}F_6$: C, 55.3; H, 4.17; P, 12.59. Found: C, 54.84; H, 4.18; P, 12.72.

$[Au_2Ir(CO)_2(PPh_3)_4]PF_6$ (3). When an acetone solution of $[Au_2Ir(H)(PPh_3)_4(NO_3)]BF_4$ (243 mg, 0.136 mmol) was placed under 1 atm of CO at -35 °C for 1 h, a very slight color change from yellow to pale yellow was observed. An orange-yellow precipitate was obtained by the addition of Et_2O at -60 °C. The solid was collected, redissolved in CH_2Cl_2, and filtered into a MeOH solution of KPF_6. A very pale yellow precipitate formed in 70% yield, which was filtered, washed with cold MeOH and Et_2O, and dried in vacuo. ^{31}P NMR (CH_2Cl_2, 25 °C): δ 43.5 (d, J_{P-P} = 71.5 Hz, assigned as AuP, int = 1), 7.6 (d, J_{P-P} = 71.5 Hz, assigned as IrP, int = 1). ^{1}H NMR (CD_2Cl_2, 25 °C): δ 6.5–8.0 (m, aromatic H), no peaks in 0 to -30 ppm region. IR (KBr): ν(CO) 1957 cm^{-1}; $\nu(PF_6)$ 840 cm^{-1}. Conductance (3 × 10^{-4} M, CH_3CN solution): 81.6 cm^2 mho mol^{-1}, indicative of a 1:1 electrolyte. FABMS (*m*-nitrobenzyl alcohol matrix): *m/e* 1691 (($Au_2Ir(CO)_2(PPh_3)_4$ = M)$^+$), 1663 ((M - CO)$^+$), 1429 ((M - PPh_3)$^+$), 1401 ((M - PPh_3 - CO)$^+$).

$\{AuRu(H)_2[P(OMe)_3]_4(PPh_3)\}NO_3$ (4). $AuPPh_3NO_3$ (142 mg, 0.273 mmol) in 3 mL of acetone was added to an acetone solution of $H_2Ru[P(OMe)_3]_4$ (163 mg, 0.271 mmol) at ambient temperature. This colorless solution was stirred for 1 h with no noticeable color change. The solvent was removed in vacuo, leaving behind a white residue, which was then redissolved in a minimal amount of CH_2Cl_2. Upon the addition of Et_2O a white microcrystalline precipitate (242 mg, 79% yield) was obtained, which was filtered, washed with Et_2O, and dried in vacuo. ^{31}P NMR (CH_2Cl_2, 25 °C): δ 45.3 (t, $J_{P-P'}$ = 31 Hz, assigned as AuP), 149.6 (t, $J_{P'-P'}$ = 53 Hz, assigned as trans RuP'), 157.3 (t of d, $J_{P-P'}$ = 53 Hz, $J_{P-P'}$ = 31 Hz, assigned as cis RuP'). ^{1}H NMR (CD_2Cl_2, 25 °C): δ -5.9 (t of t, J_{H-P} = 52.9 Hz, $J_{H-P'(cis)}$ = 19.7 Hz, $J_{H-P'(trans)}$ = 54.3 Hz based on selective ^{31}P decoupling). IR peaks were not observed in the 1800–2300-cm^{-1} region. Conductance (3 × 10^{-4} M, CH_3CN solution): 92.6 cm^2 mho mol^{-1}, indicative of a 1:1 electrolyte.

$[AuIr(H)_2(bpy)(PPh_3)_2(CH_3CN)](BF_4)_2$ was synthesized from $[Ir(H)_2(bpy)(PPh_3)_2]BF_4$ (50 mg, 0.104 mmol) in 5 mL of CH_2Cl_2 and 6 mL of CH_3CN upon the addition of $Au(CH_3CN)_2BF_4$ (80 mg, 0.22 mmol) in 5 mL of CH_3CN at 0 °C. After 10 min of stirring in the dark, Et_2O was added to precipitate a white product in 69% yield. ^{31}P NMR (CH_2Cl_2, -15 °C): δ 2.3 (s). ^{1}H NMR (CD_2Cl_2, -15 °C): δ 2.07 (s, CH_3CN), -15.61 (t, J_{P-H} = 10.4 Hz). IR (Nujol mull): ν(acetonitrile CN) 2331, 2304 (w) cm^{-1}; ν(bpy CN) 1606 (m) cm^{-1}; $\nu(BF_4)$ 1040 cm^{-1}. More complete details of this synthesis are reported elsewhere.[23]

PPh_3 Reactions. Varying amounts of PPh_3 were added to the compound of interest in the appropriate solvent at room temperature and allowed to react for a maximum to 2 h, unless otherwise noted. The reactions were monitored and determined to be quantitative by ^{31}P NMR. In some cases the product was isolated and further characterization was performed.

Results and Discussion

The reaction of PPh_3 with mixed-metal gold phosphine clusters often leads to the formation of new clusters or compounds. This reaction can therefore be of synthetic value and of some importance in an area where planned syntheses are rare. Several examples of this reaction have been reported. The addition of 1 equiv of PPh_3 to a $CHCl_3$ solution of $[Ir_3Au(\mu\text{-}H)_3(H)_3(dppe)_3(NO_3)]^+$ resulted in the rapid and complete replacement of the nitrate ligand that is bound to the gold, giving $[Ir_3Au(\mu\text{-}H)_3(H)_3(dppe)_3(PPh_3)]^{2+}$.[11] The structure of this cluster consists of a triangular array of Ir atoms with a triply bridging $AuPPh_3$ moiety and is believed to have the same arrangement of hydrides as the $AuNO_3$ adduct.[11] Upon the addition of excess PPh_3 in $CHCl_3$, however, no further reaction was observed. In contrast to this, the reaction of $[Au_2Ir(H)(PPh_3)_4(NO_3)]BF_4$ with 2 equiv of PPh_3 with use of an EtOH–Et_2O solvent mixture did give a new IrAu complex.[2] $[AuIrH(PPh_3)_4]^+$ was produced in quantitative yield along with $[Au(PPh_3)_2]^+$. The stereochemistry of $[AuIrH(PPh_3)_4]^+$ is approximately square pyramidal about the Ir atom with the $AuPPh_3$ unit occupying the axial position.[2] This second reaction in which a gold atom is extruded from the cluster has some general utility, and new examples are discussed below and shown in Figure 2.

The reaction of $[AuIr(H)(CO)(PPh_3)_4]PF_6$, the proposed stereochemistry of which is shown in Figure 2,[2] with 2 equiv of PPh_3 in CH_2Cl_2 resulted in the extrusion of the $[AuPPh_3]^+$ group. The ^{31}P NMR spectrum contained a sharp singlet at δ 12.1 and a broad singlet at δ 24.6. The former peak is due to $IrH(CO)(PPh_3)_3$,[24] while the latter peak is due to $[Au(PPh_3)_2]^+$ and PPh_3, which exchange rapidly on the NMR time scale to produce a signal that appears at the weighted average of the positions of $[Au(PPh_3)_2]^+$ (δ 42.5) and free phosphine (δ -7.8). When only 1 equiv of phosphine was used, peaks due to $[AuIr(H)(CO)(PPh_3)_4]PF_6$ and $IrH(CO)(PPh_3)_3$ were present, and a singlet at δ 35.4 due to the $[Au(PPh_3)_2]^+$–PPh_3 exchange system. The shift to lower field of the last peak is due to an increase in the amount of $[Au(PPh_3)_2]^+$ relative to that of free phosphine. Apparently this $[Au(PPh_3)_2]^+$–PPh_3 equilibrium ties up some free phosphine, resulting in the necessary addition of more than 1 equiv of PPh_3 to produce the complete reaction

$$[HIr(PPh_3)_3(AuPPh_3)(CO)]^+ + PPh_3 \rightarrow IrH(CO)(PPh_3)_3 + [Au(PPh_3)_2]^+$$

A slight molar excess of PPh_3 in CH_2Cl_2 was added to a solution of $[AuIr(H)_2(bpy)(PPh_3)_2(CH_3CN)](BF_4)_2$, a complex that is analogous to $[AuIr(H)_2(bpy)(PPh_3)_3](BF_4)_2$[2] but with the CH_3CN coordinated to Au, in CH_2Cl_2. The ^{31}P NMR spectrum taken at -80 °C showed large peaks at δ 41.6 and 19.0, due to $[Au(PPh_3)_2]^+$ and $[Ir(H)_2(bpy)(PPh_3)_2]BF_4$,[2] respectively. Also present were peaks at δ 46.3 and 3.1 due to formation of $[AuIr(H)_2(bpy)(PPh_3)_3](BF_4)_2$,[2] as well as a signal due to starting material at δ 2.27, and a peak of unknown origin at δ 7.3. Addition of a second 1 equiv of PPh_3 produced a spectrum that contained only peaks due to $[Au(PPh_3)_2]^+$ and $[Ir(H)_2(bpy)(PPh_3)_2]BF_4$. Thus, the coordinated CH_3CN was readily replaced by PPh_3 to form $[AuIr(H)_2(bpy)(PPh_3)_3](BF_4)_2$, which in turn reacted further with PPh_3 to form $[Ir(H)_2(bpy)(PPh_3)_2]BF_4$ and $[Au(PPh_3)_2]^+$. This has been confirmed by the reaction of PPh_3 with an isolated and purified sample of $[AuIr(H)_2(bpy)(PPh_3)_3](BF_4)_2$.

The reaction of $\{Au_5Re(H)_4[P(p\text{-tol})_3]_2(PPh_3)_5\}^{2+}$ with 3 equiv of PPh_3 in CH_2Cl_2 solution has been reported previously[1] and resulted in the formation of the new cluster $\{Au_4Re(H)_4[P(p\text{-tol})_3]_2(PPh_3)_4\}BPh_4$ (**1**) in good yield. The reaction involved the extrusion of a $(AuPPh_3)^+$ ion from the Au_5Re cluster and is apparently driven by the formation of $[Au(PPh_3)_2]^+$. This latter species was observed as a reaction product by ^{31}P NMR. The Au_5Re cluster is very crowded around the Re atom, which is 11-coordinate if the four hydrides are assumed to be bonded to the Re. In addition, one of the Au–Au bonds is significantly longer than the others (3.222 (1) Å vs. an average of 2.936 (1) Å).[3] Therefore, it is not surprising that one $(AuPPh_3)^+$ ion can be removed. The addition of excess PPh_3 to **1** did not result in the removal of additional gold atoms.

The structure of **1** was determined by X-ray crystallography. The structure of the coordination core with selected distances and angles is shown in Figure 1 and is seen to consist of an edge-bridged tetrahedron. The bonded Au–Au distances (average 2.857 Å, range 2.802 (2)–2.919 (2) Å), are reasonable compared with distances observed in other clusters. The significant variations in these distances are common in gold clusters due to the soft nature of the bonding. The average Au–Au bond distance in the Au_5Re cluster is much longer (2.936 Å). The Re–Au distances (average 2.726 (2) Å) are short compared with those in $\{Au_5Re(H)_4[P(p\text{-tol})_3]_2(PPh_3)_5\}(PF_6)_2$ (average 2.805 (1) Å), due to the crowded nature of this latter compound. The average Au–P and Re–P distances are 2.26 (1) and 2.41 (1) Å, respectively. The Re–P distances compare well with those in $ReH_7(PPh_3)_2$ (2.427 (1) Å)[25] but are short compared to those in the Au_5Re cluster

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(23) Alexander, B. D.; Johnson, B. J.; Johnson, S. M.; Mueting, A. M.; Boyle, P. D.; Pignolet, L. H., manuscript in preparation. Johnson, B. J. Ph.D. Dissertation, University of Minnesota, 1986.

(24) Wilkinson, G. *Inorg. Synth.* **1971**, *13*, 126.

(25) Howard, J. A. K.; Mead, K. A.; Spencer, J. L. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *C39*, 555. Teller, R. G.; Carroll, W. E.; Bau, R. *Inorg. Chim. Acta* **1984**, *87*, 121 and references cited therein.

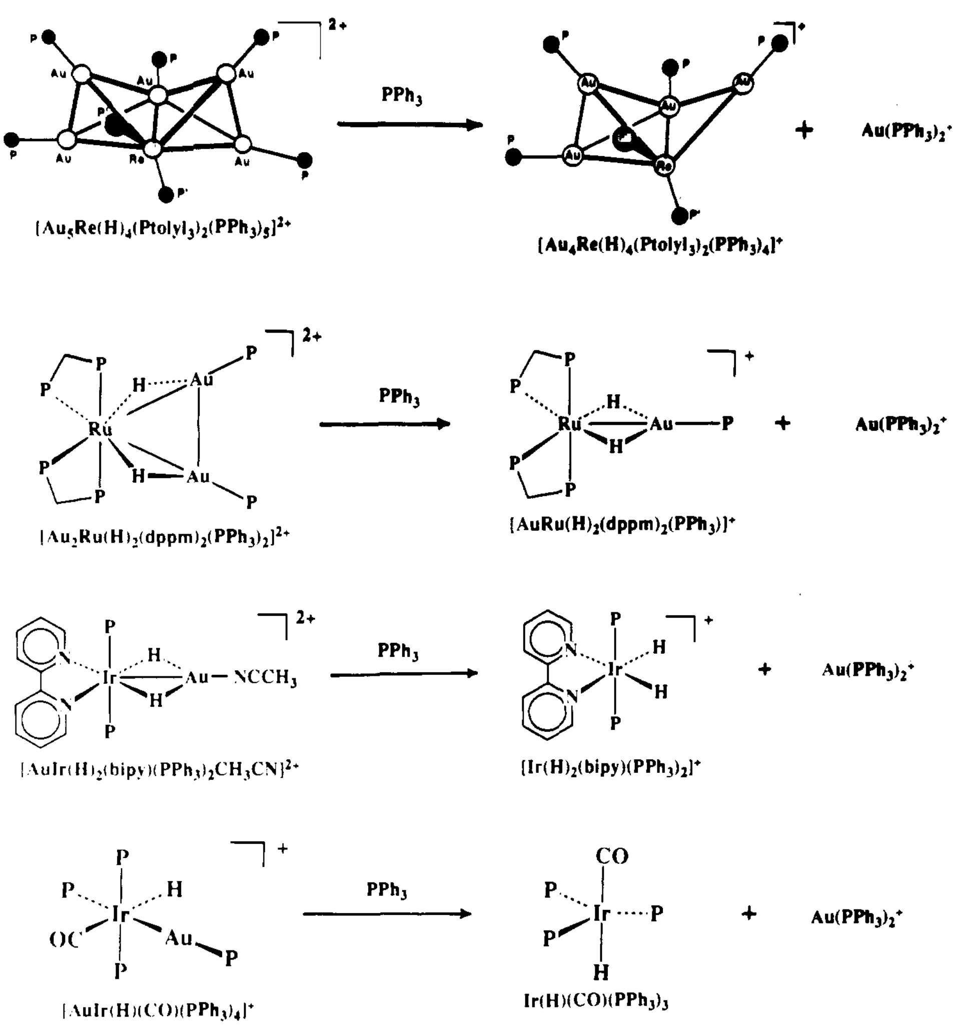


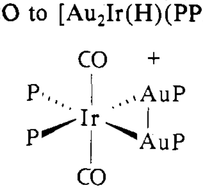
Figure 2. Scheme of cluster transformation reactions that result from the extrusion of $AuPPh_3^+$ by the addition of PPh_3. Aromatic groups have been omitted from the phosphine ligands.

(2.47 (1) Å), reflecting the decrease in the coordination number upon removal of the $AuPPh_3$ moiety. Consistent with this decrease in crowding on going from the Au_5Re to the Au_4Re cluster, the P–Re–P angle increases from 93.5 (2) to 134.0 (2)°. The Au–P vectors are all nearly trans to the Re atom (average Re–Au–P = 167.4 (2)°) as observed in the Au_5Re precursor[3] and in iridium–gold phosphine clusters in general.[2]

The addition of 1 equiv of PPh_3 to a CH_2Cl_2 solution of $[Au_2Ru(H)_2(dppm)_2(PPh_3)_2](PF_6)_2$ resulted in the extrusion of a $(AuPPh_3)^+$ ion with the formation of $[AuRu(H)_2(dppm)_2(PPh_3)]^+$ (**2**) and $[Au(PPh_3)_2]^+$. **2** has also been made via a different route, and its X-ray crystal structure has been determined, which will be reported elsewhere.[23] The solid-state structure of an isomer of **2** is shown in Figure 2. The ^{31}P NMR spectrum of $[AuRu(H)_2(dppm)_2(PPh_3)]^+$ (25 °C, CH_2Cl_2) is consistent with this solid-state structure. It consists of three multiplets of 1:2:2 integration due to the phosphorus atoms, δ 45.7 (P(A), t, J = 23.8 Hz, int = 1), 3.7 (P(B), t of d, J = 36.9 and 23.8 Hz, int = 2), and −0.3 (P(C), t, J = 36.9 Hz, int = 2). The presence of an isomer believed to have only one bridging hydride and one terminal hydride trans to the Au is evidenced by two additional singlets of 1:4 integration at δ 44.6 and 2.1. Further characterization of the two isomers of **2** will be published elsewhere.[23]

As seen in the above reactions, the apparent driving force for the extrusion of $[AuPPh_3]^+$ is the formation of $[Au(PPh_3)_2]^+$. However, reactions do not always occur, as for example in the addition of 2 equiv of PPh_3 to an isolated sample of **2**, which did not react further to form homometallic fragments. Also, the addition of an excess of PPh_3 to a CH_2Cl_2 solution of $[Au_4Ir(H)_2(PPh_3)_6]BF_4$ or $[Au_6Pt(PPh_3)_7](BPh_4)_2$ resulted in no apparent reaction within 1–2 h at room temperature. Similarly, $[Au_3Rh(H)(CO)(PPh_3)_5]^+$ did not react with 1–5 equiv of PPh_3 in either CH_2Cl_2 or 1,1,2-trichloroethane at room temperature within 2 h.

The new complex $[Au_2Ir(CO)_2(PPh_3)_4]PF_6$ (**3**) was synthesized by the addition of CO to $[Au_2Ir(H)(PPh_3)_4(NO_3)]BF_4$. The compound is believed to have the structure shown in the diagram and is based on a variety of analytical measurements (see Experimental Section). The ^{31}P NMR spectrum of this compound at room temperature showed two doublets (J = 72 Hz) at δ 43.5 and 7.6 with relative areas of 1:1. These resonances are assigned to the AuP and IrP groups, respectively. The addition of 3 equiv of PPh_3 to a CH_2Cl_2 solution of this complex at room temperature resulted in no color change. The ^{31}P NMR spectrum at −50 °C showed two very broad resonances at about δ 43 and −6, attributable to the $AuPPh_3$ ligands and free PPh_3, and a doublet at δ 7.6. This broadening was due to exchange and increased as the temperature was raised. The doublet resonance at δ 7.6 was partially coalesced due to the exchange of the Au phosphine ligands. There was no evidence of any new complex formation within 2 h, however.



3

The new compound $[AuRu(H)_2[P(OMe)_3]_4(PPh_3)]^+$ (**4**) was synthesized from the reaction of $H_2Ru[P(OMe)_3]_4$ and Au-

$(PPh_3)NO_3$. Only one isomer was observed in solution with a structure which is presumably analogous to that of **2** (see Experimental Section). The ^{31}P NMR spectrum displayed three multiplets, δ 45.3 (t, J = 31 Hz) assigned to $AuPPh_3$, δ 157.3 (t of d, J = 53 and 31 Hz) assigned to the cis $RuP(OMe)_3$ ligands, and δ 149.6 (t, J = 53 Hz) assigned to the trans $RuP(OMe)_3$ ligands. This assignment was based on comparison to $[AuRu(H)_2(dppm)_2(PPh_3)]^+$ and ^1H NMR with selective ^{31}P decoupling (see Experimental Section). The addition of 6 equiv of PPh_3 in CH_2Cl_2 at room temperature showed evidence of fast exchange between the $AuPPh_3$ ligand and free PPh_3, since the $AuPPh_3$ resonance at δ 45.3 was gone and the free PPh_3 resonance at δ -1.5 was very broad. Also, the $RuP(OMe)_3$ resonances were simplified to two triplets as a result of the loss of $AuPPh_3$ coupling. There was also evidence for cleavage of the Ru–Au bond and $(AuPPh_3)^+$ ion extrusion due to the presence of a small amount of $H_2Ru[P(OMe)_3]_4$. However, the reaction did not occur to a significant extent even over a period of 2 weeks at room temperature.

It is not readily apparent why some of these clusters were susceptible to the extrusion of gold by reaction with PPh_3 while others were not. It most likely has to do with the coordination environment of the transition metal. The number, basicity, and position of the phosphine and other ligands on the transition metal are important factors, but this is not clear as yet. Notwithstanding this, the addition of 1 equiv or more of PPh_3 is indeed a very useful way, although not entirely ubiquitous, of making new transition-metal–gold phosphine clusters.

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Registry No. **1**, 108969-20-6; **2**, 108969-22-8; **3**, 108969-24-0; **4**, 108969-26-2; $[AuIr(H)_2(bpy)(PPh_3)_2(CH_3CN)](BF_4)_2$, 108969-28-4; $\{Au_5Re(H)_4[P(p\text{-tol})_3]_2(PPh_3)_5\}(PF_6)_2$, 107742-34-7; $[Au_2Ru(H)_2(dppm)_2(PPh_3)_2](PF_6)_2$, 107712-45-8; $[Au_2Ir(H)(PPh_3)_4(NO_3)](BF_4)$, 93895-71-7; $H_2Ru[P(OMe)_3]_4$, 38784-31-5; $Au(PPh_3)NO_3$, 14897-32-6; $[Ir(H)_2(bpy)(PPh_3)_2]BF_4$, 102538-90-9; $Au(CH_3CN)_2BF_4$, 100333-93-5; $[Au_4Ir(H)_2(PPh_3)_6]BF_4$, 96705-41-8; $[Au_3Rh(H)(CO)(PPh_3)_5]PF_6$, 99595-16-1; $[Au_6Pt(PPh_3)_7](BPh_4)_2$, 107712-39-0; $[AuIr(H)(CO)(PPh_3)_4]PF_6$, 102538-86-3; $IrH(CO)(PPh_3)_3$, 17250-25-8; $[Au(PPh_3)_2]^+$, 47807-21-6; Re, 7440-15-5; Ir, 7439-88-5; Ru, 7440-18-8; PPh_3, 603-35-0; Au, 7440-57-5.

Supplementary Material Available: Tables of final atom positional and thermal parameters, all bond distances and angles in the cation, general temperature factor expressions, least-squares planes, and torsional angles for **1** and a figure showing the ORTEP representation of the cation with labeling scheme (12 pages); a table of observed and calculated structure factor amplitudes (32 pages). Ordering information is given on any current masthead page.

Notes

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^1H NMR Spin-Lattice Relaxation Studies of Hydridometal Clusters of Ruthenium and Osmium

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Although it is well established that spin–lattice relaxation times represent a powerful tool in the study of molecular dynamics and solution structures,[1] little attention has been devoted to the use of this parameter in the NMR applications to inorganic and organometallic systems.

Recently Crabtree and co-workers[2] have measured the proton relaxation times T_1 in a series of four mononuclear metal hydrido complexes showing that they are quite short (and invariably shorter than those for the other ^1H nuclei present in the compounds studied). These observations prompted us to report our results obtained on some hydrido carbonyl clusters of ruthenium and osmium (see Figure 1 and Table I); it will be also shown that the comparison of the relaxation behavior of different isotopomers may provide an extimate of the internuclear distances involving the hydrides.

To a first approximation, the observed values can be understood simply in terms of two parameters: proximity of other ^1H nuclei and molecular mobility (since, within the extreme narrowing situation, T_1 decreases as the molecular dimension increases and/or the temperature is lowered). On this basis it is likely that the spin–lattice relaxation times T_1 of the hydrido ligands are mainly determined by the efficient dipolar interactions with other nearby ^1H nuclei in the same molecule; intermoleuclar dipolar contributions seem not to be important. In the dihydrido species (**3**, **8**, **9**) we did not observe any significant difference in T_1 values for different hydride resonances in the same molecule. On the other hand, the large value observed for the sole hydride in **7**, which clearly depends on the long distance from the protons of the organic ligand, is noteworthy; an indirect location of this hydride by X-ray diffraction[3] indicates that it is bridging a

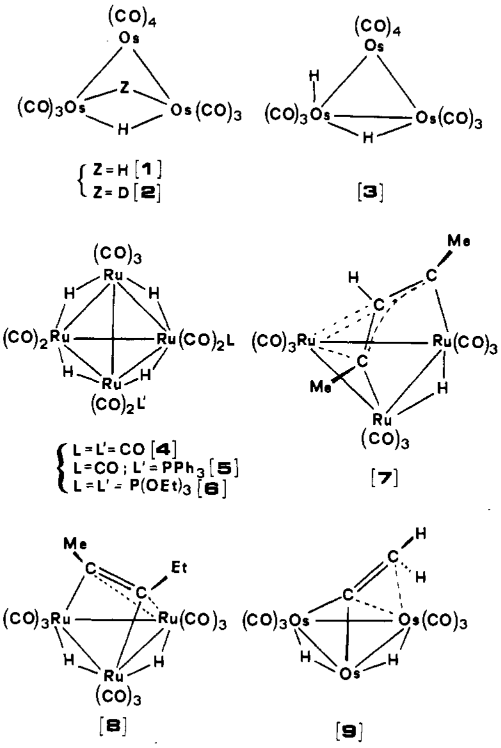

Figure 1. Structures of the hydrido clusters 1–9.

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(1) Noggle, J. E.; Schirmer, R. E. In *The Nuclear Overhauser Effect*; Academic: New York, 1971.

(2) Crabtree, R. H.; Segmuller, B. E.; Uriarte, R. J. *Inorg. Chem.* **1985**, *24*, 1949.

0020-1669/87/1326-2551$01.50/0