as well as is currently being adapted to the synthesis of other macrocycles possessing electron-rich cavities, such as: 15-[(2,6)pyridino$_5$coronand-5], as well as the pyridine analogues to "spherands".[15]

Acknowledgment. We thank the donors of the Petroleum Research Foundation, administered by the American Chemical Society, and the National Science Foundation for partial support of the initial phases of this project. Special thanks are given to Mrs. Kröhnke for the contribution of numerous dissertations from her husband's archives and to Professor Roger Laine for the special mass spectral data.

Registry No. 1, 86712-08-5; **2**, 4411-80-7; **3**, 49669-26-3; **4**, 86712-09-6; **5**, 86712-10-9; **6**, 86712-11-0; 1,3-dibromopropane, 109-64-8; 1,3-propanedithiol, 109-80-8.

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(15) Cram, D. J.; Moran, J. R.; Maverick, E. F.; Trueblood, K. N. *J. Chem. Soc., Chem. Commun.* **1983**, 645 and ref cited therein.

Reaction of $Au(NO_3)PPh_3$ with Cationic Polyhydride Cluster Complexes of Iridium(III). Structures of $[AuIr_3H_6(NO_3)(dppe)_3]BF_4$ and $[Au_3Ir(NO_3)(PPh_3)_5]PF_6$

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There have been several recent reports on mixed-metal cluster compounds that contain gold atoms.[1-5] The majority of these clusters contain carbonyl ligands, and preparative methods have primarily involved reactions between anionic metal clusters and $[AuCl(PR_3)]$ or $[Au(PR_3)]^+$ and reactions between neutral metal hydrido clusters and $[Au(CH_3)(PR_3)]$, although several other synthetic routes have also been reported.[6,7] A very recent report[8] describes the preparation and structure of a μ-H iridium–gold complex $[(PPh_3)Au(\mu\text{-}H)Ir(H)_2(PPh_3)_3]BF_4$. The above studies clearly demonstrate a structural similarity between certain hydrido–metal complexes and $AuPR_3$ derivatives. Indeed, many of the synthetic schemes for mixed-metal gold clusters have involved the replacement of a μ-H ligand and $AuPR_3$.

We report here the reactions of $Au(NO_3)PPh_3$ with $[Ir_3(\mu_3\text{-}H)(\mu\text{-}H)_3H_3(dppe)_3](BF_4)_2$ (**1**)[9] and $[Ir_2(\mu\text{-}H)_3H_2(PPh_3)_4]PF_6$ (**2**)[10] in acetone solution which yield respectively the new cationic iridium–gold clusters $[AuIr_3H_6(NO_3)(dppe)_3]BF_4$ (**3**) [dppe = $Ph_2P(CH_2)_2PPh_2$] and $[Au_3Ir(NO_3)(PPh_3)_5]PF_6$ (**4**).[11] These reactions are the first examples where *cationic* hydrido–metal complexes are converted into mixed-metal gold clusters by reaction with $AuX(PR_3)$ and illustrate that the replacement of a metallo hydrogen ligand by $AuPR_3$ is very general. In addition, complexes **3** and **4** are very rare examples of mixed-metal gold clusters that do not contain carbonyl ligands. The structure of **4** (vide infra) also illustrates a new class of gold cluster compounds since this planar "$Au_3M(PPH_3)_3$" structural unit has not been previously reported.[12]

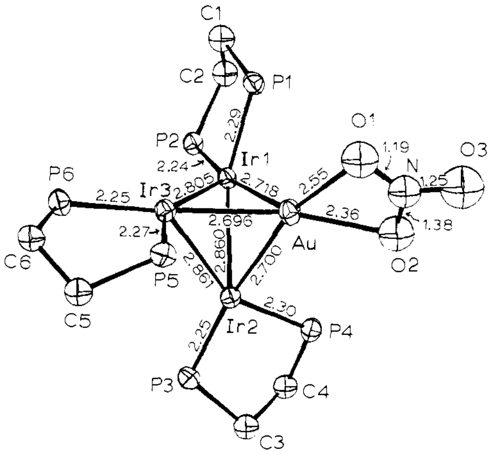
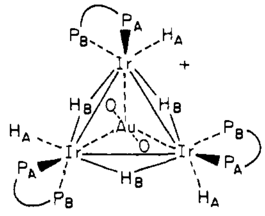


Figure 1. ORTEP drawing of the core of cation **3**. Selected angles (deg) where the numbers refer to respective Ir atoms are: 1–2–3, 58.71 (2); 1–2–Au, 58.44 (2); 3–2–Au, 57.90 (2); 2–1–3, 60.67 (2); 2–1–Au, 57.83 (2); 3–1–Au, 58.41 (2); 1–3–2, 60.62 (2); 1–3–Au, 59.18 (2); 2–3–Au, 58.05 (2); 1–Au–2, 63.73 (2); 1–Au–3, 62.41 (2); 2–Au–3, 64.05 (2); P1–1–P2, 85.4 (2); P3–2–P4, 84.6 (2); P5–3–P6, 84.2 (2); O1–Au–O2, 53.7 (6); Au–1–P2, 170.4 (1); Au–2–P3, 164.1 (1); Au–3–P6, 173.2 (1). Phenyl carbon atoms have been omitted for clarity.



3

The ^1H NMR (300 MHz, $CDCl_3$, 25 °C) spectrum of **3** in the hdyride region [δ −8.86, H_B (d, $J(P_BH_B)$ = 72 Hz) intensity = 1; −15.04, H_A (mult), intensity = 1] is very similar to that of **1** except that the quartet resonance of the μ_3-hydride is missing, and small but significant shifts in the positions of the μ-H and terminal H resonances were observed. This spectrum is consistent with the structure shown in drawing **3** where $AuNO_3$ has replaced the μ_3-hydride. The $^{31}P\{^1H\}$ NMR (120 MHz, CH_2Cl_2, 25 °C) spectrum of **3** shows two unassigned resonances: δ 44.3 ppm (br s) intensity = 1 and 32.1 (mult) intensity = 1. Addition of 1 equiv of PPh_3 to a $CHCl_3$ solution of **3** results in the rapid and complete replacement of the nitrate ligand giving $[AuIr_3H_6(PPh_3)(dppe)_3]^{2+}$

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(1) Green, M.; Orpen, A. G.; Salter, I. D.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1982**, 813. Bateman, L. W.; Green, M.; Howard, J. A. K.; Mead, K. A.; Mills, R. M.; Salter, I. D.; Stone, F. G. A.; Woodward, P. *Ibid.* **1982**, 773. Green, M. Mead, K. A.; Mills, R. M.; Salter, I. D.; Stone, F. G. A.; Woodward, P. *Ibid.* **1982**, 51.

(2) Johnson, B. F. G.; Kaner, D. A.; Lewis, J.; Raithby, P. R.; Taylor, M. J. *J. Chem. Soc., Chem. Commun.* **1982**, 314; *Polyhedron* **1982**, *1*, 105.

(3) Evans, D. G.; Mingos, D. M. P. *J. Organomet. Chem.* **1982**, *232*, 171.

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

(5) Ellis, J. E. *J. Am. Chem. Soc.* **1981**, *101*, 6106.

(6) Bruce, M. I.; Nicholson, B. K. *J. Chem. Soc., Chem. Commun.* **1982**, 1141.

(7) van der Velden, J. W. A.; Bour, J. J.; Otterloo, B. F.; Bosman, W. P.; Noordik, J. H. *J. Chem. Soc., Chem. Commun.* **1981**, 583.

(8) Lehner, H.; Matt, D.; Pregosin, P. S.; Venanzi, L. M.; Albinati, A. *J. Am. Chem. Soc.* **1982**, *104*, 6825.

(9) Wang, H. H.; Pignolet, L. H. *Inorg. Chem.* **1980**, *19*, 1470. Wang, H. H. Ph.D. Thesis, University of Minnesota, 1980.

(10) Crabtree, R. H.; Felkin, H.; Morris, G. E. *J. Organomet. Chem.* **1977**, *141*, 205.

(11) Complex **3** was prepared in ca. 35% isolated yield by the addition of 2 equiv of $AuNO_3(PPh_3)$ to 1 equiv of **1** in an acetone/dichloromethane (1:1, v/v) solution at room temperature. The yellow solution became orange after stirring for 24 h in the dark, and orange crystals were obtained via evaporation and recrystallization from $CHCl_3/Et_2O$. Complex **4** was prepared in ca. 30% isolated yield by the addition of 4 equiv of $AuNO_3(PPh_3)$ to 1 equiv of **2** in an acetone solution at room temperature. The yellow solution became dark red immediately, and crystals separated upon solvent removal.

(12) Professor J. E. Ellis has synthesized the compound $[Au_3(PPh_3)_3Mn(CO)_4]$ (Ellis, J. E.; Flatynek, R. A. *J. Am. Chem. Soc.* **1977**, *99*, 1801) and preliminary X-ray diffraction results show the presence of a very similar planar "$Au_3M(PPh_3)_3$" structural unit.

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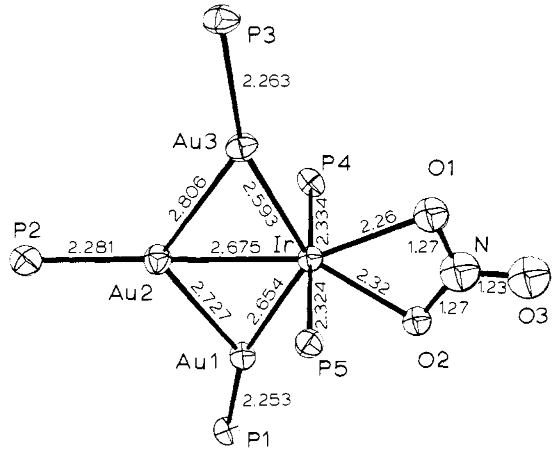

Figure 2. ORTEP drawing of the core of cation **4**. Selected angles (deg) where the numbers refer to respective Au atoms are: 1–2–3, 115.24 (3); 2–1–Ir, 59.60 (3); 2–3–Ir, 59.24 (3); 1–Ir–3, 125.90 (3); 2–1–P1, 138.0 (1); 2–3–P3, 140.1 (1); Ir–1–P1, 161.8 (1); Ir–3–P3, 160.5 (1); 1–2–P2, 122.2 (1); 3–2–P2, 122.6 (1); P4–Ir–P5, 176.6 (2); O1–Ir–O2, 57.4 (4). Phenyl carbon atoms have been omitted for clarity.

(**5**). The structure of **5** is confirmed by ^{31}P and ^{1}H NMR.[13] Complex **3** is originally isolated as the nitrate because Au(NO$_3$)PPh$_3$ undergoes ligand exchange with **5** to yield [Au(PPh$_3$)$_2$]$^+$ and **3**.

The ^{1}H NMR spectrum of complex **4** shows no resonances in the hydride region and the ^{31}P{^{1}H} NMR spectrum consists of three resonances with relative intensities of 1:2:2 [(CH$_2$Cl$_2$) δ 42.0, P2, (t, J = 9.5 Hz) intensity = 1; 13.7 (mult) intensity = 2; −4.43 (t, J = 7.5 Hz) intensity = 2]. The assignment of the resonances at 13.7 and −4.43 ppm is, at present, unknown. This spectrum is consistent with the structure shown in Figure 2. NMR monitoring of the reaction mixture shows the presence of several additional species. Efforts are under way to crystallize these other compounds especially because a new polyhydride species is evident.[14]

In order to verify the structures of these compounds and to add to our understanding of the structural features of mixed-metal gold clusters, we determined the single-crystal X-ray structures of **3** and **4**.[15] The molecular structures of the cations are shown in Figures 1 and 2 along with selected bond lengths and angles. The structure of **3** consists of an approximate AuIr$_3$ tetrahedron. The internal M–M–M angles are all very near 60° (max, min = 64.1°, 57.8°). The M–M bond distances (av Ir–Ir = 2.842 (1) Å, av Ir–Au = 2.705 (1) Å) are significantly different, however. The Ir–Au distances are short while the Ir–Ir distances are longer than those in the similar μ_3-H compound [Ir$_3$(μ_3–H)(μ–H)$_3$(H)$_3$(dppp)$_3$]$^{2+}$ [dppp = Ph$_2$P(CH$_2$)$_3$PPh$_2$].[9] The Ir–P bond lengths reflect the positioning of the hydride ligands (see drawing of **3**). Thus the Ir–P bonds that are trans to μ-H ligands are lengthened [av Ir–P = 2.287 (4) Å] relative to the ones that are trans to the Au atom [av Ir–P = 2.245 n(4) Å]. This latter distance is identical with that found in the μ_3-H dppp analogue [av Ir–P = 2.243 (2) Å][9] and illustrates the electronic similarity between μ_3-H and μ_3-Au. In support of this the geometry of the Ir$_3$H$_6$(dppe)$_3$ grouping in **3** is very similar to that of the analogous μ_3-H complex [Ir$_3$(μ_3-H)(μ-H)$_3$(H)$_3$(dppp)$_3$]$^{2+}$.[9]

The structure of **4** consists of a nearly planar Au$_3$Ir grouping with deviations from the least-squares plane of +0.011 Å for Au2 and Ir and −0.013 Å for Au1 and Au3. In addition, P2 and the entire NO$_3$ group lie approximately within this plane, while P1 and P3 are displaced −0.19 and −0.13 Å, respectively, from this plane. The Ir–P4 and Ir–P5 vectors are orthogonal to this plane. The three gold atoms are bonded to the Ir atom with unusually short bond distances (av Au–Ir = 2.641 (1) Å) and Au1 and Au3 are bonded to Au2 in a bent arrangement [Au1–Au2–Au3 115.24 (3)°]. The Au–Au separations [av 2.767 (1) Å] are typical of other gold cluster complexes.[16]

A more detailed account of the synthetic and crystallographic details will appear at a later date.

Acknowledgment is made to the National Science Foundation (NSF Grant CHE 81-08490 to L.H.P.) and to NATO for a travel grant to J.J.S. and L.H.P. The Johnson-Matthey Co. is acknowledge for a generous loan of IrCl$_3$. A.L.C. is the recipient of an NSF Graduate Fellowship.

Supplementary Material Available: Tables of positional and thermal parameters for the cations **3** and **4** (6 pages). Ordering information is given on any current masthead page.

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[13] ^{31}P{^{1}H} NMR of **5** (CDCl$_3$) δ 81.7 (q, J = 38 Hz) intensity = 1, 43.1 (br d) intensity = 3, 41.5 (d, J = 38 Hz) intensity = 3; ^{1}H NMR δ −6.79 (d, J = 74 Hz) intensity = 1, −13.4 (mult) intensity = 1.

[14] Two of these species have been identified as [Au(PPh$_3$)$_2$]$^+$ and [Au$_9$(PPh$_3$)$_8$]$^{3+}$ by ^{31}P NMR, and a new polyhydride species is observed by ^{1}H NMR [(acetone) δ −7.80 (t, J = 54.9 Hz), −23.6(s)].

[15] Compound **3**·3CHCl$_3$ (unstable in the absence of solvent, C$_{81}$H$_{81}$AuIr$_3$P$_6$NO$_3$BF$_4$Cl$_9$, M_c = 2471.04) crystallizes in the triclinic space group $P1$, with a = 13.656(3), b = 14.310 (3), c = 13.234 (2) Å; α = 95.88 (2), β = 116.06 (3), γ = 71.77 (2)°; Z = 1, V = 2205 (1) Å^3; ρ_c = 1.861 g cm^{-3}. 9607 independent reflections were collected (up to $2\theta_{max} < 54°$), of which 7048 were considered as observed [$F_o^2 \geq 3.0\sigma(F_o^2)$] and subsequently used. The structure converged to the present conventional R factor of 0.061 by using anisotropic thermal parameters of Au, Ir, and P atoms and isotropic for the others. Compound **4** (C$_{90}$H$_{75}$Au$_3$IrP$_6$NO$_3$F$_6$, M_c = 2301.54) crystallizes in the monoclinic space group $P2_1/c$, with a = 14.042 (3), b = 13.309 (2)8 c = 43.58 (1) Å; β = 91.07 (2)°; Z = 4, V = 8143 (5) Å$_3$; ρ_c = 1.877 g cm^{-3}. 8689 independent reflections were collected (up to $2\theta_{max} < 42°$), of which 4896 were considered as observed [$F_o^2 \geq 2.0\sigma(F_o^2)$] and subsequently used. The structure converged to the present conventional R factor of 0.056 by using anisotropic thermal parameters for Au, Ir, P, and F atoms. Data for both compounds were collected on an Enraf Nonius CAD 4 diffractometer at room temperature (Mo K$\bar{\alpha}$ λ = 0.71069 Å, graphite monochromated) by using an $\omega/2\theta$ scan for **3** and an ω scan for **4**. Both structures were refined using full-matrix least-squares analysis, and data were corrected for the effects of absorption and anomalous dispersion Scattering factors were taken from the "International Tables for X-ray Crystallography", Vol. IV.

[16] Steggerda, J. J.; Bour, J. J.; van der Velden, J. W. A. *Recl. Trav. Chim. Pays*-Bas **1982**, *101*, 164.

Synthesis and Transilience of a 1,3-Diazabiphenylene

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In the course of our studies of coenzyme–enzyme interactions using dimensional probes,[1] we became interested in the synthesis and chemical properties of 1,3-diazabiphenylenes. We recently reported[1a] the first synthesis of this ring system by a thermal (780 °C) nitrogen extrusion in the gas phase, and we now wish to communicate an alternative synthesis via a diethynylpyrimidine utilizing the cobalt-catalyzed cooligomerization methods developed by Vollhardt.[2] We also wish to report an unusual, high-yield structural rearrangement of this diazabiphenylene to an isoquinoline with formal elimination of HCN.

The synthesis begins with 4,6-dichloro-5-formylpyrimidine, which is readily available from 4,6-dihydroxypyrimidine.[3] Elaboration of the aldehyde to the dibromoalkene **1** with CBr$_4$/

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[1] (a) Leonard, N. J. *Acc. Chem. Res.* **1982**, *15*, 128–135 and references therein, including: (b) Leonard, N. J.; Morrice, A. G.; Sprecker, M. A. *J. Org. Chem.* **1975**, *40*, 356–363, 363–366. (c) Leonard, N. J.; Sprecker, M. A.; Morrice, A. G. *J. Am. Chem. Soc.* **1976**, *98*, 3987–3994. (d) Scopes, D. I. C.; Barrio, J. R.; Leonard, N. J. *Science* (*Washington, D.C.*) **1977**, *195*, 296–298. (e) Leonard, N. J.; Scopes, D. I. C.; VanDerLijn, P.; Barrio, J. R. *Biochemistry* **1978**, *17*, 3677–3685. (f) Keyser, G. E.; Leonard, N. J. *J. Org. Chem.* **1979**, *44*, 2989–2994. (g) Moder, K. P.; Leonard, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 2613–2624.

[2] (a) Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1–8. (b) Berris, B. C.; Lai, Y.-H.; Vollhardt, K. P. C. *J. Chem. Soc., Chem. Commun.* **1982**, 953–954. (c) Brien, D. J.; Naiman, A.; Vollhardt, K. P. C. *Ibid.* **1982**, 133–134.

[3] Klotzer, W.; Herberz, M. *Monatsh. Chem.* **1965**, *96*, 1567–1578.

0002-7863/83/1505-5958$01.50/0