

was filtered, the resin was washed with  $\text{CH}_2\text{Cl}_2$  (two times, 50 mL), and the washings and filtrate were combined for IR and plasma emission analysis. The recovered resin was treated five times in an analogous manner. The resin that was left after six such treatments was washed with  $\text{CH}_2\text{Cl}_2$  and analyzed for Rh and Co. Analyses are given in Table II.

**Registry No.**  $\text{Co}_4(\text{CO})_{12}$ , 17786-31-1;  $\text{Co}(\text{CO})_4^-$ , 14971-27-8;  $\text{Rh}_2(\text{CO})_{30}^{2-}$ , 12775-50-7;  $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$ , 50696-78-1;  $\text{Rh}_4(\text{CO})_{12}$ , 19584-30-6;  $\text{Rh}_4(\text{CO})_2\text{Cl}_2^-$ , 15550-00-2;  $\text{Rh}(\text{CO})_4^-$ , 44797-04-8;  $[(\text{Bu}_4\text{N}^+)_2(\text{Co}(\text{CO})_4^-)]^+$ , 87739-34-2;  $[(\text{Bu}_4\text{N}^+)_2(\text{Rh}(\text{CO})_2(\text{Cl})_2^-)]^+$ , 87739-35-3;  $\text{Ir}_2\text{Co}_2(\text{CO})_{12}$ , 50696-80-5;  $\text{Ir}_2\text{Cl}_2(\text{C}_8\text{H}_{14})_4$ , 12246-51-4;  $\text{NaCo}(\text{CO})_4$ , 14878-28-5;  $\text{Cl}^-$ , 16887-00-6.

## Cluster Chemistry. 27.<sup>1</sup> The Synthesis and Structural Characterization of Three Mixed Gold-Cobalt-Ruthenium Carbonyl Clusters $\text{Ph}_3\text{PAuCoRu}_3(\text{CO})_{13}$ , $(\text{Ph}_3\text{PAu})_2\text{CoRu}_3(\text{H})(\text{CO})_{12}$ , and $(\text{Ph}_3\text{PAu})_3\text{CoRu}_3(\text{CO})_{12}$

Michael I. Bruce\* and Brian K. Nicholson\*<sup>2</sup>

Jordan Laboratories, Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia 5001, Australia

Received August 2, 1983

A unique series of mixed gold-cobalt-ruthenium carbonyl clusters has been prepared and structurally characterized. Reaction of  $[(\text{Ph}_3\text{PAu})_3\text{O}]\text{BF}_4$  with  $\text{HCoRu}_3(\text{CO})_{13}$  gives the three clusters  $\text{Ph}_3\text{PAuCoRu}_3(\text{CO})_{13}$  (1),  $(\text{Ph}_3\text{PAu})_2\text{CoRu}_3(\text{H})(\text{CO})_{12}$  (2), and  $(\text{Ph}_3\text{PAu})_3\text{CoRu}_3(\text{CO})_{12}$  (3). An alternative specific route to 3 is via  $[(\text{Ph}_3\text{PAu})_3\text{O}]\text{BF}_4$  and  $[\text{CoRu}_3(\text{CO})_{13}]^-$ , while  $\text{Ph}_3\text{PAuCl}$  and  $[\text{CoRu}_3(\text{CO})_{13}]^-$  give exclusively 1. For 1 [ $\text{C}_{31}\text{H}_{15}\text{O}_{13}\text{AuCoPRu}_3$ ,  $a = 9.345$  (3) Å,  $b = 14.217$  (4) Å,  $c = 14.721$  (3) Å,  $\alpha = 114.83$  (2)°,  $\beta = 93.16$  (2)°,  $\gamma = 92.44$ °, triclinic,  $\bar{P}1$ ,  $Z = 2$ ] a trigonal-bipyramidal core is found, with the  $\text{Ph}_3\text{PAu}$  group triply bridging a  $\text{CoRu}_2$  triangle. For 2 [ $\text{C}_{48}\text{H}_{31}\text{Au}_2\text{CoO}_{12}\text{P}_2\text{Ru}_3 \cdot 0.5\text{CH}_2\text{Cl}_2$ ,  $a = 35.173$  (9) Å,  $b = 13.548$  (9) Å,  $c = 23.193$  (4) Å,  $\beta = 102.27$  (2)°, monoclinic,  $C2/c$ ,  $Z = 8$ ] a capped trigonal-bipyramidal core exists with the second  $\text{Ph}_3\text{PAu}$  group capping an  $\text{AuRu}_2$  face of 1 and the hydride ligand bridging an  $\text{Ru-Ru}$  bond. The structures are rationalized in terms of the maximum number of face-sharing tetrahedra; the isolobality of H and  $\text{Ph}_3\text{PAu}$  is not valid in the context of polygold clusters.

### Introduction

Development of the burgeoning field of mixed-metal clusters is limited by some practical difficulties. First, specific syntheses of the higher nuclearity clusters are not commonly available. Secondly, there are very few series of closely related clusters differing in nuclearity so that the effects of increasing size cannot be readily measured.

A number of groups have recently reported syntheses of mixed-metal clusters containing gold atoms by (i) the addition of  $\text{R}_3\text{PAu}^+$  to appropriate cluster anions<sup>3-10</sup> and

(ii) by the elimination of  $\text{CH}_4$  between  $\text{R}_3\text{PAuMe}$  and cluster hydrides.<sup>11</sup> For (i) only one or two Au atoms have been introduced since most cluster anions are only mono- or dinegatively charged, although Ellis has reported  $\text{V}(\text{AuPPh}_3)_3(\text{CO})_5$  via the  $[\text{V}(\text{CO})_5]^{3-}$  anion.<sup>12</sup> We have adopted a different approach in our current efforts, namely, the use of the strong aurating agent  $(\text{Ph}_3\text{PAu})_3\text{O}^+$  first reported by Nesmeyanov et al.,<sup>13</sup> which we have found can add up to three gold atoms to a cluster substrate.<sup>14,15</sup>

(1) For Part 26, see: Bruce, M. I.; Williams, M. L.; Nicholson, B. K., submitted for publication in *J. Organomet. Chem.*

(2) On leave from the University of Waikato, Hamilton, New Zealand, where correspondence should be addressed.

(3) Lewis, J.; Johnson, B. F. G. *Pure Appl. Chem.* 1982, 54, 97.

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

(5) (a) Johnson, B. F. G.; Kaner, D. A.; Lewis, J.; Raithby, P. R.; Taylor, M. J. *Polyhedron* 1982, 1, 105. (b) Burgess, K.; Johnson, B. F. G.; Kaner, D. A.; Lewis, J.; Raithby, P. R.; Syed-Mustaffa, S. N. A. B. *J. Chem. Soc., Chem. Commun.* 1983, 455. (c) Johnson, B. F. G.; Lewis, J.; Nicholls, J. N.; Puga, J.; Whitmire, K. H. *J. Chem. Soc., Dalton Trans.* 1983, 787. (d) Johnson, B. F. G.; Lewis, J.; Nelson, W. J. H.; Raithby, P. R.; Vargas, M. D. *J. Chem. Soc., Chem. Commun.* 1983, 608.

(6) Johnson, B. F. G.; Kaner, D. A.; Lewis, J.; Raithby, P. R. *J. Organomet. Chem.* 1981, 215, C33; *J. Chem. Soc., Chem. Commun.* 1981, 753.

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

(8) (a) Braunstein, P.; Rose, J.; Dusausoy, Y.; Mangelot, J. P. *C. R. Seances Acad. Sci., Ser. 2* 1982, 294, 967. (b) Braunstein, P.; Predieri, G.; Tiripicchio, A.; Sappa, E. *Inorg. Chim. Acta* 1982, 63, 113.

(9) (a) Johnson, B. F. G.; Kaner, D. A.; Lewis, J.; Raithby, P. R.; Rosales, M. J. *J. Organomet. Chem.* 1982, 231, C59. (b) Johnson, B. F. G.; Kaner, D. A.; Lewis, J.; Rosales, M. J. *Ibid.* 1982, 238, C73. (c) Johnson, B. F. G.; Lewis, J.; Nelson, W. J. H.; Puga, J.; Raithby, P. R.; Braga, D.; McPartlin, M.; Clegg, W. *Ibid.* 1983, 243, C13.

(10) Mays, M. J.; Raithby, P. R.; Taylor, P. L.; Henrick, K. *J. Organomet. Chem.* 1982, 224, C45.

(11) (a) Bateman, L. W.; Green, M.; Howard, J. A. K.; Mead, K. A.; Mills, R. M.; Salter, I. D.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* 1982, 773. (b) Green, M.; Mead, K. A.; Mills, R. M.; Salter, I. D.; Stone, F. G. A.; Woodward, P. *Ibid.* 1982, 51. (c) Farrugia, L. J.; Howard, J. A. K.; Mitrprachachon, P.; Spencer, J. L.; Stone, F. G. A.; Woodward, P. *Ibid.* 1978, 260. (d) Bateman, L. W.; Green, M.; Mead, K. A.; Mills, R. M.; Slater, I. D.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.*, in press.

(12) Ellis, J. E. *J. Am. Chem. Soc.* 1981, 103, 6106.

(13) Nesmeyanov, A. N.; Perevalova, E. G.; Struchkov, Y. T.; Antipin, M. Y.; Grandberg, K. I.; Dyadchenko, V. P. *J. Organomet. Chem.* 1980, 201, 343.

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

(15) Bruce, M. I.; Nicholson, B. K. *J. Organomet. Chem.* 1983, 252, 243.

Table I. Summary of Crystal Structure Data

	1	2
formula	C <sub>31</sub> H <sub>15</sub> O <sub>13</sub> AuCoPRu <sub>3</sub>	C <sub>46</sub> H <sub>31</sub> Au <sub>2</sub> CoO <sub>12</sub> P <sub>2</sub> Ru <sub>3</sub> ·~0.5CH <sub>2</sub> Cl <sub>2</sub>
M <sub>r</sub>	1185.5	1660.2
cryst origin	CH <sub>2</sub> Cl <sub>2</sub> /hexane	CH <sub>2</sub> Cl <sub>2</sub> /hexane
cryst form	deep red needle	black needle
cryst size, mm	0.39 × 0.08 × 0.06	0.40 × 0.13 × 0.07
cryst system	triclinic	monoclinic
space group	P $\bar{1}$	C2/c
a, Å	9.345 (3)	35.173 (9)
b, Å	14.217 (4)	13.548 (9)
c, Å	14.721 (3)	23.193 (4)
α, deg	114.83 (2)	90
β, deg	93.16 (2)	102.27 (2)
γ, deg	92.44 (2)	90
U, Å <sup>3</sup>	1767	10799
Z	2	8
D <sub>calcd</sub> , g cm <sup>-3</sup>	2.228	2.042
D <sub>measd</sub> , g cm <sup>-3</sup>	2.20 (2)	2.02 (2)
F(000)	1116	6264
μ(Mo Kα), cm <sup>-1</sup>	59	68
radiant	graphite monochromated Mo Kα, λ = 0.7107 Å	
scan type	ω <sup>-1</sup> /θ	ω <sup>-2</sup> /θ
horizontal aperture, mm	2.4 + 0.5 tan θ	2.4 + 0.8 tan θ
ω scan angle, deg	1.0 + 0.35 tan θ	0.8 + 0.35 tan θ
2θ range, deg	3-45	3-36
total data	5078	6700
unique data	4175	3615
data, I > 2.5σ(I)	3332	2874
final R and R <sub>w</sub>	0.037 and 0.038	0.046 and 0.052
weight w = 1.0[σ <sup>2</sup> (F <sub>o</sub> ) + pF <sub>o</sub> <sup>2</sup> ] <sup>-1</sup>	p = 0.0004	p = 0.0009

We now wish to report the use of this gold oxonium reagent to prepare mixed gold-cobalt-ruthenium clusters from the readily available<sup>16</sup> [CoRu<sub>3</sub>(CO)<sub>13</sub>]<sup>-</sup> or HCoRu<sub>3</sub>(CO)<sub>13</sub>. We also compare in detail the structures of Ph<sub>3</sub>PAuCoRu<sub>3</sub>(CO)<sub>13</sub> (1), (Ph<sub>3</sub>PAu)<sub>2</sub>CoRu<sub>3</sub>(H)(CO)<sub>12</sub> (2), and (Ph<sub>3</sub>PAu)<sub>3</sub>CoRu<sub>3</sub>(CO)<sub>12</sub> (3), which contain metal cores [Au<sub>x</sub>CoRu<sub>3</sub>] (x = 1-3) of stepwise increasing nuclearity. Preliminary details and the structure of 3 have been communicated previously.<sup>14</sup>

### Experimental Section

**General Comments.** All reactions were carried out in standard Schlenk equipment under dry nitrogen. Tetrahydrofuran was freshly distilled from sodium-benzophenone before use while other reagent grade solvents were used without purification. Petroleum spirit refers to a 40-60 °C boiling fraction. Preparative scale chromatography was carried out on 20 × 20 cm plates coated with silica gel (Merck, PF<sub>254</sub>). The starting materials Na[CoRu<sub>3</sub>(CO)<sub>13</sub>],<sup>16</sup> PPN[CoRu<sub>3</sub>(CO)<sub>13</sub>],<sup>16</sup> HCoRu<sub>3</sub>(CO)<sub>13</sub>,<sup>16</sup> and [(Ph<sub>3</sub>PAu)<sub>3</sub>O]BF<sub>4</sub><sup>+</sup><sup>13</sup> were prepared by literature procedures. Infrared spectra were recorded on a Perkin-Elmer 683 double-grating spectrometer and are accurate to ±1 cm<sup>-1</sup>; <sup>1</sup>H NMR spectra were obtained on a Bruker WP80 instrument. Analyses were performed by Canadian Microanalytical Service, Vancouver.

**Preparation of Ph<sub>3</sub>PAuCoRu<sub>3</sub>(CO)<sub>13</sub> (1).** A solution of [CoRu<sub>3</sub>(CO)<sub>13</sub>]<sup>-</sup> (prepared in situ from Ru<sub>3</sub>(CO)<sub>12</sub> (0.30 g, 0.47 mmol) and NaCo(CO)<sub>4</sub> (0.5 mmol) in 10 mL of THF) was treated with solid Ph<sub>3</sub>PAuCl (0.24 g, 0.47 mmol). After 10 min at room temperature solvent was removed in vacuo and the residue was dissolved in 5 mL of CH<sub>2</sub>Cl<sub>2</sub>. Petroleum spirit (10 mL) was added and the mixture cooled to -30 °C to deposit black crystals of Ph<sub>3</sub>PAuCoRu<sub>3</sub>(CO)<sub>13</sub> (1): 0.251 g, 45%; IR (hexane) 2086 (w), 2041 (vs), 1982 (m, br), 1899 (w), 1858 (w) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.20 (m, Ph<sub>3</sub>P). Anal. Calcd for C<sub>31</sub>H<sub>15</sub>O<sub>13</sub>AuCoPRu<sub>3</sub>: C, 31.40; H, 1.28. Found: C, 31.07; H, 1.14. The compound was further characterized by a full crystal structure analysis. (See below.)

**Preparation of (Ph<sub>3</sub>PAu)<sub>3</sub>CoRu<sub>3</sub>(CO)<sub>12</sub> (3).** A mixture of PPN[CoRu<sub>3</sub>(CO)<sub>13</sub>] (0.05 g, 0.04 mmol) and [(Ph<sub>3</sub>PAu)<sub>3</sub>O]BF<sub>4</sub> (0.054 g, 0.036 mmol) was stirred in 10 mL of THF for 2 h. Solvent was removed in vacuo and the residue extracted with 5 mL of benzene. Petroleum spirit was added to the benzene solution and the mixture cooled to -30 °C to give black crystals of (Ph<sub>3</sub>PAu)<sub>3</sub>CoRu<sub>3</sub>(CO)<sub>12</sub> (3) as a benzene solvate: 0.047 g, 55%; IR (CH<sub>2</sub>Cl<sub>2</sub>) 2058 (s), 2014 (s), 2000 (s), 1984 (m), 1956 (m), 1840 (w), 1810 (w) cm<sup>-1</sup>. Anal. Calcd for C<sub>46</sub>H<sub>45</sub>O<sub>12</sub>Au<sub>3</sub>CoP<sub>3</sub>Ru<sub>3</sub>C<sub>6</sub>H<sub>6</sub>: C, 40.15; H, 2.40. Found: C, 40.02; H, 1.54. The cluster was also characterized by a full crystal structure analysis. The residue from the benzene extraction was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O to give off-white crystals of PPN<sup>+</sup>BF<sub>4</sub><sup>-</sup> (by IR), 0.019 g, 85%.

**Reaction of HCoRu<sub>3</sub>(CO)<sub>13</sub> with [(Ph<sub>3</sub>PAu)<sub>3</sub>O]BF<sub>4</sub>.** A mixture of HCoRu<sub>3</sub>(CO)<sub>13</sub> (0.10 g, 0.14 mmol) and [(Ph<sub>3</sub>PAu)<sub>3</sub>O]BF<sub>4</sub> (0.10 g, 0.067 mmol) in 8 mL of THF was stirred for 1-2 h. Solvent was removed under vacuum and the residue run on preparative scale thin-layer chromatography plates. Elution with benzene/petroleum spirit (1:1) gave three major bands, other than traces of Ru<sub>3</sub>(CO)<sub>12</sub> and HCoRu<sub>3</sub>(CO)<sub>13</sub> which moved virtually with the solvent front. Band 1 (brown; R<sub>f</sub> 0.90) was identified as Ph<sub>3</sub>PAuCoRu<sub>3</sub>(CO)<sub>13</sub> by comparison with an authentic sample. Band 2 (red-brown; R<sub>f</sub> 0.5) was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/petroleum spirit to give black needles of (Ph<sub>3</sub>PAu)<sub>2</sub>CoRu<sub>3</sub>(H)(CO)<sub>12</sub>·0.5CH<sub>2</sub>Cl<sub>2</sub> (2): 0.02 g, 9%; IR (CH<sub>2</sub>Cl<sub>2</sub>) 2069 (s), 2026 (vs), 2008 (s), 1968 (m), 1830 (w, br) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.32 (m, Ph<sub>3</sub>P), 5.29 (s, CH<sub>2</sub>Cl<sub>2</sub>), -11.6 (s, MH). Anal. Calcd for C<sub>48.5</sub>H<sub>32</sub>O<sub>12</sub>Au<sub>2</sub>ClCoP<sub>2</sub>Ru<sub>3</sub>: C, 35.09; H, 1.94. Found: C, 35.48; H, 0.44. The cluster was also characterized by a structure analysis. (See below.) Band 3 (purple-brown; R<sub>f</sub> 0.20; 0.072 g, 25%) was identified as Au<sub>3</sub>CoRu<sub>3</sub>(CO)<sub>12</sub>(PPh<sub>3</sub>)<sub>3</sub> (3) by comparison with an authentic sample.

**Crystallography.** The structure of 3 has been previously described.<sup>14</sup> Suitable crystals of 1 and 2 were mounted on an Enraf-Nonius CAD4 diffractometer, and the lattice parameters were determined by using 25 high-angle reflections. Data are summarized in Table I. Space group P $\bar{1}$  was assumed for 1, and this choice was confirmed by the successful analysis. For 2 data were collected on the basis of a triclinic cell and transformed to the correct monoclinic cell when the higher symmetry became apparent during solution of the structure.

For each of the analyses the positions of the metal atoms were found by direct methods, with other non-hydrogen atoms being located in subsequent difference maps. In the final cycles of

(16) (a) Steinhardt, P. C.; Gladfelter, W. G.; Harley, A. D.; Fox, J. R.; Geoffroy, G. L. *Inorg. Chem.* 1980, 19, 332. (b) Roberts, D. A.; Harley, A. D.; Geoffroy, G. L. *Organometallics* 1982, 1, 1050. (c) Geoffroy, G. L.; Fox, J. R.; Burkhardt, E.; Foley, H. C.; Harley, A. D.; Rosen, R. *Inorg. Synth.* 1982, 21, 61.

Table II. Positional Parameters for  $\text{Ph}_3\text{PAuCoRu}_3(\text{CO})_{13}$  ( $\times 10^4$ )

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Au(1)	3515 (1)	5744 (1)	7754 (1)
Ru(1)	4518 (1)	3806 (1)	6672 (1)
Ru(2)	1445 (1)	4296 (1)	6414 (1)
Ru(3)	2223 (1)	2263 (1)	6027 (1)
Co	2511 (1)	3869 (1)	7876 (1)
P	4093 (3)	7476 (2)	8782 (2)
C(1)	4466 (13)	3738 (9)	8128 (9)
C(2)	570 (14)	4153 (9)	7646 (9)
C(3)	1973 (13)	2501 (8)	7578 (8)
O(1)	5283 (10)	3661 (10)	8707 (8)
O(2)	-516 (11)	4172 (10)	7993 (9)
O(3)	1650 (12)	1960 (7)	7958 (7)
C(11)	4805 (12)	3781 (9)	5387 (11)
C(12)	6097 (12)	4865 (9)	7249 (10)
C(13)	5671 (12)	2660 (9)	6340 (9)
C(21)	804 (11)	5694 (10)	6936 (10)
C(22)	2008 (12)	4384 (10)	5246 (11)
C(23)	-346 (12)	3654 (8)	5761 (9)
C(31)	3243 (13)	1093 (8)	5924 (9)
C(32)	2434 (16)	2067 (9)	4685 (9)
C(33)	381 (13)	1546 (8)	5728 (10)
O(11)	5115 (10)	3777 (8)	4655 (7)
O(12)	7136 (9)	5361 (7)	7529 (8)
O(13)	6429 (10)	2014 (7)	6156 (8)
O(21)	300 (10)	6457 (7)	7142 (9)
O(22)	2220 (11)	4458 (9)	4504 (9)
O(23)	-1447 (10)	3317 (7)	5367 (8)
O(31)	3806 (10)	360 (7)	5805 (8)
O(32)	2607 (16)	1879 (9)	3876 (8)
O(33)	-695 (11)	1071 (7)	5506 (10)
C(41)	2304 (13)	4423 (9)	9180 (10)
O(41)	2125 (13)	4737 (8)	9998 (7)
C(51)	6007 (5)	7820 (5)	8955 (6)
C(52)	6852 (5)	7377 (5)	9452 (6)
C(53)	8332 (5)	7557 (5)	9548 (6)
C(54)	8969 (5)	8180 (5)	9148 (6)
C(55)	8125 (5)	8623 (5)	8651 (6)
C(56)	6645 (5)	8443 (5)	8554 (6)
C(61)	3521 (7)	7914 (5)	10053 (4)
C(62)	4214 (7)	8756 (5)	10860 (4)
C(63)	3701 (7)	9085 (5)	11801 (4)
C(64)	2495 (7)	8571 (5)	11936 (4)
C(65)	1802 (7)	7730 (5)	11129 (4)
C(66)	2315 (7)	7401 (5)	10187 (4)
C(71)	3284 (7)	8301 (5)	8266 (5)
C(72)	2638 (7)	9195 (5)	8845 (5)
C(73)	2013 (7)	9779 (5)	8399 (5)
C(74)	2033 (7)	9469 (5)	7374 (5)
C(75)	2678 (7)	8575 (5)	6794 (5)
C(76)	3303 (7)	7991 (5)	7240 (5)

blocked full-matrix least-squares refinement the phenyl rings were treated as rigid groups ( $d_{\text{C-C}} = 1.395 \text{ \AA}$ ) with hydrogen atoms at calculated positions ( $d_{\text{C-H}} = 0.95 \text{ \AA}$ ). For 1 all atoms other than those of the phenyl rings were treated anisotropically, while for 2 only the Au, Co, Ru, and P atoms were assigned anisotropic temperature factors. Refinement proceeded straightforwardly for 1; for 2 the  $\text{CH}_2\text{Cl}_2$  did not refine well and was included as a disordered, half-weighted carbon and four quarter-weighted chlorine atoms with a common temperature factor. This gave a tolerable, although not ideal, refinement. For 2 the hydrido H atom was not located. There was no evidence for extinction, and no anomalous peaks were apparent in final electron density maps.

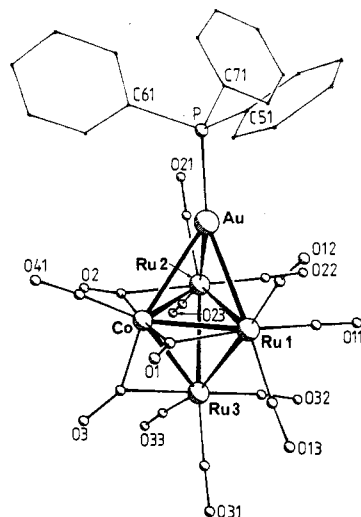
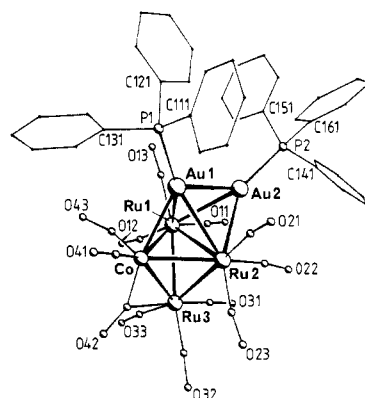
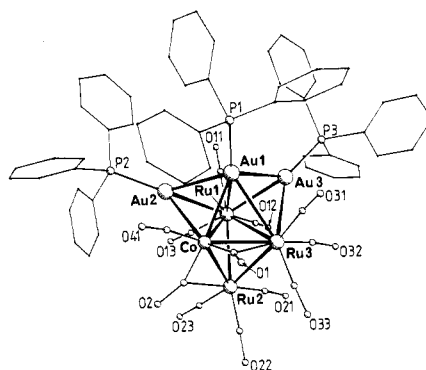
The neutral atomic scattering factors used were those of Cromer and Mann,<sup>17</sup> and anomalous scattering was included. Calculations were performed by using SHELX 76,<sup>18</sup> except for absorption corrections which employed ABSORB,<sup>19</sup> in a Gaussian integration procedure. Diagrams were prepared by using PLUTO.<sup>20</sup>

(17) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* 1968, 24A, 321.

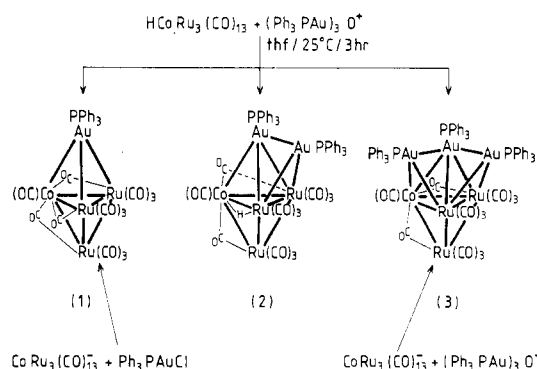
(18) Sheldrick, G. SHELX, University of Cambridge, 1976.

(19) ABSORB, University of Sydney, 1976.

(20) PLUTO, S. Motherwell, University of Cambridge, 1976.

Figure 1. A perspective view of  $\text{Ph}_3\text{PAuCoRu}_3(\text{CO})_{13}$ .Figure 2. A perspective view of  $(\text{Ph}_3\text{PAu})_2\text{CoRu}_3(\text{H})(\text{CO})_{12}$ .Figure 3. A perspective view of  $(\text{Ph}_3\text{PAu})_3\text{CoRu}_3(\text{CO})_{12}$ .

## Scheme I



Final positional parameters (Tables II and III), bond lengths (Tables IV and V), and bond angles (Tables VI and VII) are given

Table III. Positional Parameters for  $(\text{Ph}_3\text{PAu})_2\text{CoRu}_3(\text{H})(\text{CO})_{12}$  ( $\times 10^4$ )

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Au(1)	1088 (1)	3181 (1)	3818 (1)
Au(2)	1556 (1)	3178 (1)	2987 (1)
Ru(1)	1579 (1)	4895 (1)	3752 (1)
Ru(2)	910 (1)	4441 (1)	2756 (1)
Ru(3)	1080 (1)	6391 (1)	3172 (1)
Co(1)	835 (1)	5057 (2)	3872 (1)
P(1)	994 (2)	1808 (4)	4332 (3)
P(2)	1915 (2)	1990 (14)	2650 (3)
C(11)	1944 (6)	4972 (17)	3275 (8)
C(12)	1811 (7)	5985 (15)	4200 (10)
C(13)	1856 (6)	3932 (17)	4270 (9)
C(21)	704 (7)	3211 (17)	2546 (10)
C(22)	1190 (6)	4520 (15)	2146 (9)
C(23)	497 (7)	5132 (17)	2316 (11)
C(31)	1415 (7)	6563 (16)	2677 (11)
C(32)	690 (6)	7099 (16)	2710 (9)
C(33)	1277 (7)	7453 (19)	3650 (11)
C(41)	463 (9)	4608 (22)	4142 (12)
C(42)	661 (7)	6261 (17)	3766 (9)
C(43)	1173 (7)	5101 (16)	4504 (10)
O(11)	2190 (5)	5049 (12)	3027 (7)
O(12)	1990 (5)	6581 (11)	4503 (7)
O(13)	2053 (5)	3455 (12)	4610 (7)
O(21)	526 (5)	2521 (14)	2355 (8)
O(22)	1328 (5)	4643 (11)	1749 (7)
O(23)	230 (5)	5445 (13)	1985 (8)
O(31)	1606 (5)	6656 (11)	2320 (7)
O(32)	441 (5)	7611 (12)	2426 (7)
O(33)	1410 (5)	8157 (12)	3895 (7)
O(41)	204 (6)	4340 (14)	4359 (9)
O(42)	447 (5)	6861 (12)	3901 (8)
O(43)	1322 (4)	4794 (11)	36 (7)
C(111)	663 (4)	922 (9)	3917 (5)
C(112)	725 (4)	-95 (9)	3951 (5)
C(113)	445 (4)	-734 (9)	3637 (5)
C(114)	104 (4)	-356 (9)	3288 (5)
C(115)	42 (4)	662 (9)	3253 (5)
C(116)	322 (4)	1301 (9)	3567 (5)
C(121)	1427 (3)	1092 (9)	4645 (6)
C(122)	1447 (3)	505 (9)	5145 (6)
C(123)	1774 (3)	-083 (9)	5348 (6)
C(124)	2080 (3)	-084 (9)	5052 (6)
C(125)	2060 (3)	503 (9)	4552 (6)
C(126)	1733 (3)	1091 (9)	4349 (6)
C(131)	784 (4)	2082 (11)	4957 (6)
C(132)	479 (4)	1541 (11)	5099 (6)
C(133)	326 (4)	1812 (11)	5583 (6)
C(134)	477 (4)	2624 (11)	5925 (6)
C(135)	782 (4)	3165 (11)	5783 (6)
C(136)	936 (4)	2894 (11)	5299 (6)
C(141)	2091 (4)	2374 (10)	2004 (5)
C(142)	1829 (4)	2478 (10)	1464 (5)
C(143)	1961 (4)	2784 (10)	966 (5)
C(144)	2355 (4)	2986 (10)	1009 (5)
C(145)	2617 (4)	2882 (10)	1549 (5)
C(146)	2485 (4)	2576 (10)	2046 (5)
C(151)	2338 (3)	1624 (10)	3194 (5)
C(152)	2505 (3)	689 (10)	3200 (5)
C(153)	2852 (3)	477 (10)	3598 (5)
C(154)	3032 (3)	1201 (10)	3991 (5)
C(155)	2866 (3)	2136 (10)	3985 (5)
C(156)	2519 (3)	2348 (10)	3586 (5)
C(161)	1650 (4)	865 (8)	2422 (6)
C(162)	1316 (4)	681 (8)	2637 (6)
C(163)	1099 (4)	-174 (8)	2469 (6)
C(164)	1218 (4)	-845 (8)	2086 (6)
C(165)	1553 (4)	-662 (8)	1872 (6)
C(166)	1769 (4)	193 (8)	2039 (6)
Cl(1)	750 (7)	3411 (19)	749 (10)
Cl(2)	927 (8)	2018 (21)	138 (12)
Cl(3)	695 (7)	1306 (17)	661 (10)
Cl(4)	604 (7)	2656 (19)	1042 (11)
C(1)	643 (18)	2700 (48)	463 (28)

Table IV. Bond Lengths for  $\text{Ph}_3\text{PAuCoRu}_3(\text{CO})_{13}$  (Å)

Au(1)-Ru(1)	2.776 (1)	Co-C(1)	1.88 (1)
Au(1)-Ru(2)	2.774 (1)	Co-C(2)	1.92 (1)
Au(1)-Co	2.868 (2)	Co-C(3)	1.85 (1)
Ru(1)-Ru(2)	3.025 (1)	Co-C(41)	1.77 (1)
Ru(1)-Ru(3)	2.818 (1)	C(1)-O(1)	1.16 (2)
Ru(1)-Co	2.631 (2)	C(2)-O(2)	1.16 (2)
Ru(2)-Ru(3)	2.837 (1)	C(3)-O(3)	1.16 (2)
Ru(2)-Co	2.629 (2)	C(11)-O(11)	1.13 (2)
Ru(3)-Co	2.710 (1)	C(12)-O(12)	1.12 (1)
Au(1)-P	2.305 (2)	C(13)-O(13)	1.13 (2)
Ru(1)-C(11)	1.91 (2)	C(21)-O(21)	1.13 (2)
Ru(1)-C(12)	1.94 (1)	C(22)-O(22)	1.17 (2)
Ru(1)-C(13)	1.90 (1)	C(23)-O(23)	1.13 (1)
Ru(1)-C(1)	2.19 (2)	C(31)-O(31)	1.14 (2)
Ru(2)-C(21)	1.94 (1)	C(32)-O(32)	1.13 (2)
Ru(2)-C(22)	1.88 (2)	C(33)-O(33)	1.14 (2)
Ru(2)-C(23)	1.88 (1)	C(41)-O(41)	1.13 (2)
Ru(2)-C(2)	2.11 (1)	P-C(51)	1.810 (6)
Ru(3)-C(31)	1.91 (1)	P-C(61)	1.826 (7)
Ru(3)-C(32)	1.90 (1)	P-C(71)	1.813 (9)
Ru(3)-C(33)	1.89 (1)		
Ru(3)-C(3)	2.19 (1)		

Table V. Bond Lengths for  $(\text{Ph}_3\text{PAu})_2\text{CoRu}_3(\text{H})(\text{CO})_{12}$  (Å)

Au(2)-Au(1)	2.787 (1)	Co(1)-C(42)	1.742 (23)
Ru(1)-Au(1)	2.915 (2)	Ru(1)-C(43)	2.494 (22)
Ru(2)-Au(1)	2.953 (2)	Co(1)-C(43)	1.679 (24)
Co(1)-Au(1)	2.704 (3)	C(11)-O(11)	1.139 (21)
P(1)-Au(1)	2.272 (5)	C(12)-O(12)	1.164 (23)
Ru(1)-Au(2)	2.916 (2)	C(13)-O(13)	1.136 (21)
Ru(2)-Au(2)	2.803 (2)	C(21)-O(21)	1.159 (24)
P(2)-Au(2)	2.285 (5)	C(22)-O(22)	1.140 (20)
Ru(2)-Ru(1)	2.989 (2)	C(23)-O(23)	1.158 (26)
Ru(3)-Ru(1)	2.826 (2)	C(31)-O(31)	1.179 (24)
Co(1)-Ru(1)	2.697 (3)	C(32)-O(32)	1.199 (22)
Ru(3)-Ru(2)	2.833 (2)	C(33)-O(33)	1.156 (25)
Co(1)-Ru(2)	2.786 (3)	C(41)-O(41)	1.188 (29)
Co(1)-Ru(3)	2.691 (3)	C(42)-O(42)	1.192 (23)
Ru(1)-C(11)	1.868 (21)	C(43)-O(43)	1.241 (23)
Ru(1)-C(12)	1.889 (24)	P(1)-C(111)	1.800 (12)
Ru(1)-C(13)	1.897 (22)	P(1)-C(121)	1.822 (12)
Ru(2)-C(21)	1.840 (24)	P(1)-C(131)	1.797 (13)
Ru(2)-C(22)	1.891 (21)	P(2)-C(141)	1.815 (12)
Ru(2)-C(23)	1.845 (26)	P(2)-C(151)	1.803 (12)
Ru(3)-C(31)	1.826 (26)	P(2)-C(161)	1.806 (11)
Ru(3)-C(32)	1.824 (23)	C-Cl(1)	1.185 (62)
Ru(3)-C(33)	1.858 (27)	C-Cl(2)	1.656 (63)
Co(1)-C(41)	1.679 (31)	C-Cl(3)	1.944 (66)
Ru(3)-C(42)	2.230 (22)	C-Cl(4)	1.381 (60)

for 1 and 2 while thermal parameters and structure factor amplitudes are available as supplementary material.

## Results

**Synthesis.** When  $\text{HCoRu}_3(\text{CO})_{13}$  and  $[(\text{Ph}_3\text{PAu})_3\text{O}]\text{BF}_4$  are reacted together, a mixture of the three clusters 1-3 is formed (Scheme I); these can be readily separated by TLC on silica gel. The relative amounts of the three products vary with the proportions of the two reactants so that 1 is the dominant species at low oxonium to cluster ratios, while 3 predominates at high ratios. Under all stoichiometries 2 remains a relatively minor product. The appearance of all three products early in the reaction and the presence of 1 and 2 even after long reaction times with excess oxonium salt preclude a simple stepwise buildup of the clusters. A similar pattern of reactivity was found for the related  $\text{H}_4\text{Ru}_4(\text{CO})_{12}/[(\text{Ph}_3\text{PAu})_3\text{O}]^+$  system.<sup>15</sup> A mechanistic proposal must await further studies.

Alternative routes to 1 and 3 have been developed. Thus a straightforward reaction between  $[\text{CoRu}_3(\text{CO})_{13}]^-$  and  $\text{Ph}_3\text{PAuCl}$  gave 1 in good yields, in a procedure directly analogous to those used by other groups to prepare simple gold derivatives of other clusters.<sup>3-10</sup> Similarly a mixture

Table VI. Bond Angles for  $\text{Ph}_3\text{PAuCoRu}_3(\text{CO})_{13}$  (deg)

Ru(2)-Au(1)-Ru(1)	66.1 (1)	C(2)-Co-C(41)	89.0 (6)	Ru(3)-Co-Au(1)	110.4 (1)
Co-Au(1)-Ru(1)	55.5 (1)	Co-C(1)-Ru(1)	80.2 (5)	Ru(3)-Co-Ru(2)	64.2 (1)
Co-Au(1)-Ru(2)	55.5 (1)	Ru(1)-C(1)-O(1)	136.9 (11)	C(51)-P-C(61)	104.7 (3)
P-Au(1)-Ru(1)	146.8 (1)	Co-C(1)-O(1)	142.8 (12)	C(51)-P-C(71)	106.5 (4)
P-Au(1)-Ru(2)	145.7 (1)	Co-C(3)-Ru(3)	83.9 (6)	C(61)-P-C(71)	105.9 (3)
P-Au(1)-Co	139.9 (1)	Ru(3)-C(3)-O(3)	134.5 (8)	C(12)-Ru(1)-C(11)	88.9 (6)
Ru(1)-Ru(2)-Au(1)	57.0 (1)	Ru(1)-C(12)-O(12)	169.9 (10)	C(11)-Ru(1)-C(13)	88.3 (6)
Co-Ru(2)-Au(1)	64.1 (1)	Ru(2)-C(21)-O(21)	171.3 (10)	C(21)-Ru(2)-C(23)	94.6 (6)
Co-Ru(2)-Ru(3)	59.3 (1)	Ru(2)-C(23)-O(23)	176.3 (12)	C(31)-Ru(3)-C(32)	95.0 (6)
Co-Ru(3)-Ru(1)	56.8 (1)	Ru(3)-C(32)-O(32)	174.5 (14)	C(32)-Ru(3)-C(33)	94.4 (6)
Ru(1)-Co-Au(1)	60.5 (1)	Co-C(41)-O(41)	176.6 (12)	C(1)-Co-C(41)	90.2 (6)
Ru(2)-Co-Ru(1)	70.2 (1)	Ru(2)-Ru(1)-Au(1)	56.9 (1)	C(3)-Co-C(41)	99.1 (6)
Ru(3)-Co-Ru(1)	63.7 (1)	Ru(3)-Ru(1)-Au(1)	110.0 (1)	Co-C(2)-Ru(2)	81.3 (5)
Au(1)-P-C(51)	113.0 (3)	Ru(3)-Ru(1)-Ru(2)	58.0 (1)	Ru(2)-C(2)-O(2)	140.6 (12)
Au(1)-P-C(61)	115.0 (1)	Co-Ru(1)-Au(1)	64.0 (1)	Co-C(2)-O(2)	138.0 (13)
Au(1)-P-C(71)	111.2 (1)	Co-Ru(1)-Ru(2)	54.9 (1)	Co-C(3)-O(3)	141.6 (9)
C(11)-Ru(1)-C(1)	172.3 (5)	Co-Ru(1)-Ru(3)	59.5 (1)	Ru(1)-C(11)-O(11)	173.2 (10)
C(12)-Ru(1)-C(13)	95.7 (5)	Ru(3)-Ru(2)-Ru(1)	57.3 (1)	Ru(1)-C(13)-O(13)	176.0 (10)
C(21)-Ru(2)-C(22)	91.8 (6)	Co-Ru(2)-Ru(1)	54.9 (1)	Ru(2)-C(22)-O(22)	173.3 (11)
C(22)-Ru(2)-C(23)	90.8 (6)	Ru(2)-Ru(3)-Ru(1)	64.7 (1)	Ru(3)-C(31)-O(31)	175.7 (10)
C(31)-Ru(3)-C(33)	95.1 (5)	Co-Ru(3)-Ru(2)	56.5 (1)	Ru(3)-C(33)-O(33)	176.2 (10)
C(2)-Co-C(1)	173.9 (6)	Ru(2)-Co-Au(1)	60.4 (1)		

Table VII. Bond Angles for  $(\text{Ph}_3\text{PAu})_2\text{CoRu}_3(\text{H})(\text{CO})_{12}$  (deg)

Ru(1)-Au(1)-Au(2)	61.5 (1)	Au(2)-Ru(2)-Au(1)	57.8 (1)	Ru(2)-Co(1)-Ru(1)	66.0 (1)
Ru(2)-Au(1)-Au(2)	58.4 (1)	Ru(1)-Ru(2)-Au(1)	58.8 (1)	Ru(3)-Co(1)-Au(1)	116.9 (1)
Ru(2)-Au(1)-Ru(1)	61.2 (1)	Ru(1)-Ru(2)-Au(2)	60.4 (1)	Ru(3)-Co(1)-Ru(1)	63.3 (1)
Co(1)-Au(1)-Au(2)	106.4 (1)	Ru(3)-Ru(2)-Au(1)	105.2 (1)	Ru(3)-Co(1)-Ru(2)	62.3 (1)
Co(1)-Au(1)-Ru(1)	57.2 (1)	Ru(3)-Ru(2)-Au(2)	113.6 (1)	C(41)-Co(1)-Au(1)	88.1 (10)
Co(1)-Au(1)-Ru(2)	58.8 (1)	Ru(3)-Ru(2)-Ru(1)	58.0 (1)	C(41)-Co(1)-Ru(1)	149.1 (10)
P(1)-Au(1)-Au(2)	122.4 (1)	Co(1)-Ru(2)-Au(1)	56.1 (1)	C(41)-Co(1)-Ru(2)	118.2 (10)
P(1)-Au(1)-Ru(1)	146.5 (2)	Co(1)-Ru(2)-Au(2)	103.8 (1)	C(41)-Co(1)-Ru(3)	147.4 (10)
P(1)-Au(1)-Ru(2)	151.9 (2)	Co(1)-Ru(2)-Ru(1)	55.6 (1)	C(42)-Co(1)-Au(1)	169.4 (7)
P(1)-Au(1)-Co(1)	131.2 (1)	Co(1)-Ru(2)-Ru(3)	57.2 (1)	C(42)-Co(1)-Ru(1)	112.5 (7)
Ru(1)-Au(2)-Au(1)	61.4 (1)	C(21)-Ru(2)-Au(1)	72.5 (7)	C(42)-Co(1)-Ru(2)	104.4 (7)
Ru(2)-Au(2)-Au(1)	63.8 (1)	C(21)-Ru(2)-Au(2)	75.9 (7)	C(42)-Co(1)-Ru(3)	55.6 (7)
Ru(2)-Au(2)-Ru(1)	63.0 (1)	C(21)-Ru(2)-Ru(1)	126.3 (7)	C(42)-Co(1)-C(41)	96.5 (12)
P(2)-Au(2)-Au(1)	133.5 (1)	C(21)-Ru(2)-Ru(3)	167.7 (7)	C(43)-Co(1)-Au(1)	84.0 (8)
P(2)-Au(2)-Ru(1)	145.5 (1)	C(21)-Ru(2)-Co(1)	114.0 (7)	C(43)-Co(1)-Ru(1)	64.7 (8)
P(2)-Au(2)-Ru(2)	148.2 (1)	C(22)-Ru(2)-Au(1)	127.2 (6)	C(43)-Co(1)-Ru(2)	129.2 (8)
Au(2)-Ru(1)-Au(1)	57.1 (1)	C(22)-Ru(2)-Au(2)	69.4 (6)	C(43)-Co(1)-Ru(3)	104.2 (8)
Ru(2)-Ru(1)-Au(1)	60.0 (1)	C(22)-Ru(2)-Ru(1)	96.7 (6)	C(43)-Co(1)-C(41)	98.7 (12)
Ru(2)-Ru(1)-Au(2)	56.7 (1)	C(22)-Ru(2)-Ru(3)	95.5 (6)	C(43)-Co(1)-C(42)	104.7 (10)
Ru(3)-Ru(1)-Au(1)	106.4 (1)	C(22)-Ru(2)-Co(1)	147.7 (6)	C(111)-P(1)-Au(1)	114.5 (5)
Ru(3)-Ru(1)-Au(2)	110.4 (1)	C(22)-Ru(2)-C(21)	95.3 (9)	C(121)-P(1)-Au(1)	116.2 (5)
Ru(3)-Ru(1)-Ru(2)	58.2 (1)	C(23)-Ru(2)-Au(1)	139.2 (7)	C(121)-P(1)-C(111)	104.4 (7)
Co(1)-Ru(1)-Au(1)	57.5 (1)	C(23)-Ru(2)-Au(2)	158.0 (7)	C(131)-P(1)-Au(1)	112.6 (5)
Co(1)-Ru(1)-Au(2)	103.1 (1)	C(23)-Ru(2)-Ru(1)	136.2 (7)	C(131)-P(1)-C(111)	103.9 (7)
Co(1)-Ru(1)-Ru(2)	58.4 (1)	C(23)-Ru(2)-Ru(3)	78.4 (7)	C(131)-P(1)-C(121)	103.9 (7)
Co(1)-Ru(1)-Ru(3)	58.3 (1)	C(23)-Ru(2)-Co(1)	98.2 (7)	C(141)-P(2)-Au(2)	113.0 (5)
C(11)-Ru(1)-Au(1)	124.4 (6)	C(23)-Ru(2)-C(21)	95.4 (10)	C(151)-P(2)-Au(2)	112.9 (5)
C(11)-Ru(1)-Au(2)	67.6 (6)	C(23)-Ru(2)-C(22)	91.9 (9)	C(151)-P(2)-C(141)	106.4 (7)
C(11)-Ru(1)-Ru(2)	94.7 (6)	Ru(2)-Ru(3)-Ru(1)	63.8 (1)	C(161)-P(2)-Au(2)	114.0 (5)
C(11)-Ru(1)-Ru(3)	96.5 (6)	Co(1)-Ru(3)-Ru(1)	58.5 (1)	C(161)-P(2)-C(141)	104.2 (7)
C(11)-Ru(1)-Co(1)	149.5 (6)	Co(1)-Ru(3)-Ru(2)	60.5 (1)	C(161)-P(2)-C(151)	105.7 (7)
C(12)-Ru(1)-Au(1)	141.7 (6)	C(31)-Ru(3)-Ru(1)	88.4 (7)	O(11)-C(11)-Ru(1)	174.0 (20)
C(12)-Ru(1)-Au(2)	155.7 (7)	C(31)-Ru(3)-Ru(2)	91.3 (7)	O(12)-C(12)-Ru(1)	171.8 (19)
C(12)-Ru(1)-Ru(2)	139.7 (7)	C(31)-Ru(3)-Co(1)	142.9 (7)	O(13)-C(13)-Ru(1)	171.0 (19)
C(12)-Ru(1)-Ru(3)	81.5 (7)	C(32)-Ru(3)-Ru(1)	165.9 (7)	O(21)-C(21)-Ru(2)	169.0 (22)
C(12)-Ru(1)-Co(1)	101.2 (7)	C(32)-Ru(3)-Ru(2)	102.2 (7)	O(22)-C(22)-Ru(2)	172.3 (18)
C(12)-Ru(1)-C(11)	90.6 (9)	C(32)-Ru(3)-Co(1)	114.2 (7)	O(23)-C(23)-Ru(2)	169.8 (22)
C(13)-Ru(1)-Au(1)	69.5 (6)	C(32)-Ru(3)-C(31)	93.9 (9)	O(31)-C(31)-Ru(3)	174.5 (21)
C(13)-Ru(1)-Au(2)	77.3 (6)	C(33)-Ru(3)-Ru(1)	99.0 (8)	O(32)-C(32)-Ru(3)	176.2 (19)
C(13)-Ru(1)-Ru(2)	124.2 (6)	C(33)-Ru(3)-Ru(2)	161.9 (8)	O(33)-C(33)-Ru(3)	172.6 (22)
C(13)-Ru(1)-Ru(3)	167.9 (6)	C(33)-Ru(3)-Co(1)	106.6 (7)	O(41)-C(41)-Co(1)	175.6 (27)
C(13)-Ru(1)-Co(1)	111.7 (6)	C(33)-Ru(3)-C(31)	93.9 (10)	Co(1)-C(42)-Ru(3)	84.3 (9)
C(13)-Ru(1)-C(11)	95.0 (8)	C(33)-Ru(3)-C(32)	94.7 (10)	O(42)-C(42)-Ru(3)	130.1 (18)
C(13)-Ru(1)-C(12)	94.9 (9)	C(42)-Ru(3)-Ru(1)	94.3 (6)	O(42)-C(42)-Co(1)	145.5 (19)
C(43)-Ru(1)-Au(1)	67.6 (5)	C(42)-Ru(3)-Ru(2)	91.0 (6)	Co(1)-C(43)-Ru(1)	77.8 (9)
C(43)-Ru(1)-Au(2)	124.7 (5)	C(42)-Ru(3)-Co(1)	40.1 (6)	Cl(2)-C(1)-Cl(1)	123.7 (49)
C(43)-Ru(1)-Ru(2)	95.2 (6)	C(42)-Ru(3)-O(31)	177.0 (9)	Cl(3)-C(1)-Cl(1)	130.8 (48)
C(43)-Ru(1)-Ru(3)	82.1 (5)	C(42)-Ru(3)-C(32)	83.7 (9)	Cl(3)-C(1)-Cl(2)	62.0 (25)
C(43)-Ru(1)-Co(1)	37.5 (6)	C(42)-Ru(3)-C(33)	84.5 (9)	Cl(4)-C(1)-Cl(1)	64.9 (35)
C(43)-Ru(1)-C(11)	167.4 (8)	Ru(1)-Co(1)-Au(1)	65.3 (1)	Cl(4)-C(1)-Cl(2)	127.8 (45)
C(43)-Ru(1)-C(12)	76.8 (8)	Ru(2)-Co(1)-Au(1)	65.1 (1)	Cl(4)-C(1)-Cl(3)	75.6 (31)
C(43)-Ru(1)-C(13)	85.8 (8)				

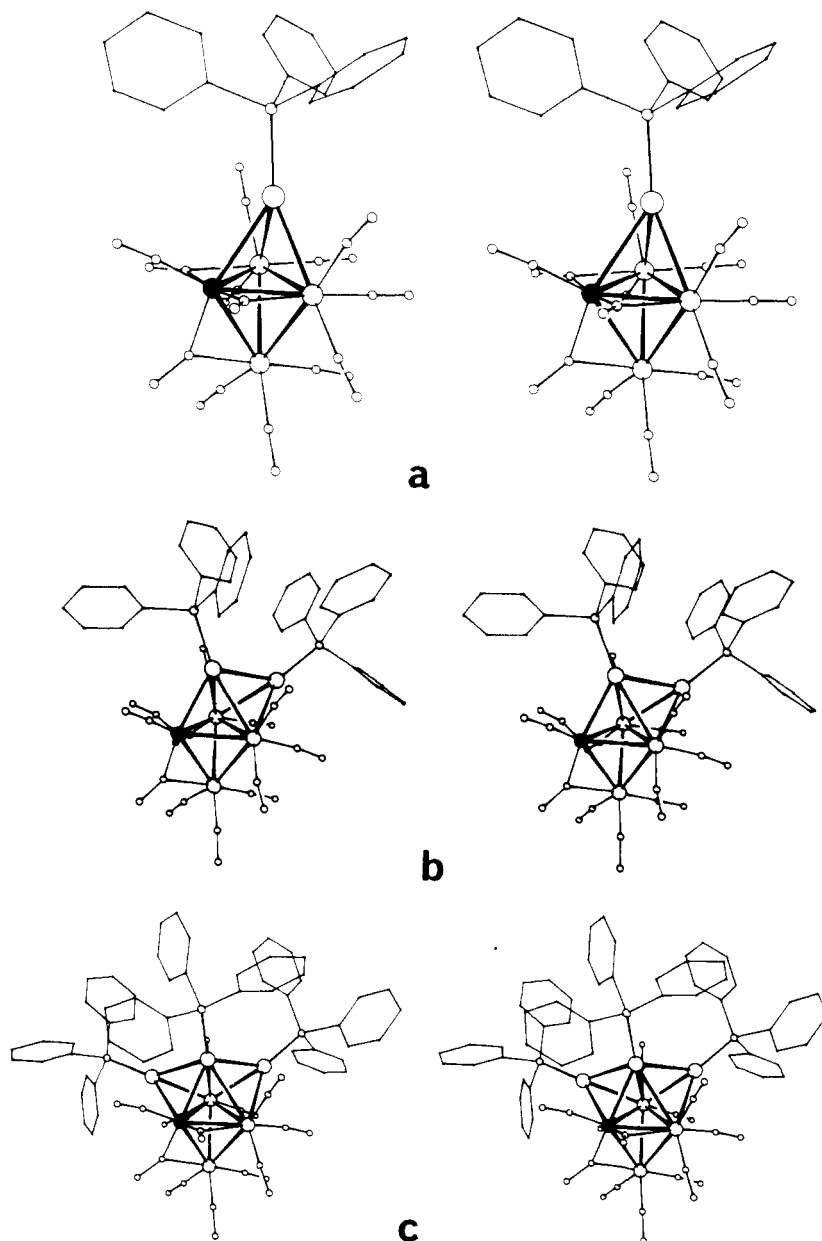
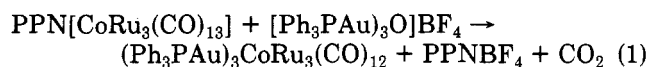


Figure 4. Stereoviews of (a) 1, (b) 2, and (c) 3.

of  $\text{PPN}[\text{CoRu}_3(\text{CO})_{13}]$  and  $[(\text{Ph}_3\text{PAu})_3\text{O}]\text{BF}_4$  gave specifically the trigold derivative 3—only traces of 1 are formed. The fate of the oxonium oxygen in this reaction is not known. However, one possibility for which a simple balanced equation can be written is that it combines with the eliminated CO to give  $\text{CO}_2$  (eq 1).



The three clusters 1–3 form black, air-stable crystals that give intense brown solutions in polar organic solvents. Solutions are stable enough to survive chromatography, but some decomposition occurs on prolonged exposure to air.

The carbonyl region solution infrared spectra are relatively simple and provide a ready means of identification. For each of 1–3 there are absorptions attributable to bridging carbonyl groups suggesting that the solution structures do not differ greatly from those found in the solid state (see below). As the degree of substitution by  $\text{Ph}_3\text{PAu}$  groups increases from 1  $\rightarrow$  3 there is a definite trend toward lower frequencies for the CO absorption

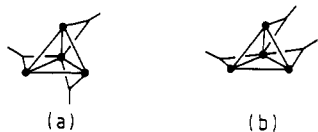
bands, indicating that the gold groups are electron-releasing overall toward the  $\text{CoRu}_3$  part of the molecules.

**The Structure of  $\text{Ph}_3\text{PAuCoRu}_3(\text{CO})_{13}$ .** Molecules of 1 consist of a trigonal-bipyramidal  $\text{AuCoRu}_3$  core, where the Au atom has capped a  $\text{CoRu}_2$  face of the original tetrahedral  $[\text{CoRu}_3(\text{CO})_{13}]^-$  precursor. The product is therefore directly comparable to  $\text{Ph}_3\text{PAuRuCo}_3(\text{CO})_{12}$  and its Fe analogue.<sup>7,8</sup> There is a  $\text{PPh}_3$  group attached to the Au atom, and three terminal CO groups are attached to each Ru atom. The Co atom has one terminal CO group, and three other CO groups unsymmetrically bridge each of the Co–Ru bonds (Co–C = 1.85–1.91 Å, Ru–C = 2.11–2.19 Å). The structure is related to that<sup>16</sup> of the precursor anion  $[\text{CoRu}_3(\text{CO})_{13}]^-$ , with similar bond lengths for the Co–Ru, two of the Ru–Ru, and the Co–C and Ru–C bonds. The Au–Ru bonds (2.775 Å) are similar to those in other  $\mu\text{-AuRu}_2$  units while the Au–Co bond is long (2.868 Å) compared to the Au–Co distances in  $\text{Ph}_3\text{PAuCo}_3\text{Ru}(\text{CO})_{12}$  (2.72 Å (av))<sup>7</sup> or in  $\text{Ph}_3\text{PAuCo}(\text{CO})_4$  (2.50 Å)<sup>21</sup> so that the  $\text{Ph}_3\text{PAu}$  group in 1 appears to be halfway between

(21) Blundell, T. L.; Powell, H. M. *J. Chem. Soc. A* 1971, 1685.

a fully  $\mu_3$  and a  $\mu$  (Ru-Ru) bridging configuration. A similar asymmetry is found for the capping AuPPh<sub>3</sub> group in Ph<sub>3</sub>PAuRu<sub>3</sub>C(CO)<sub>15</sub>(NO).<sup>9c</sup> At the same time the Ru(1)-Ru(2) distance is exceptionally long at 3.025 Å (see below).

In the anion [CoRu<sub>3</sub>(CO)<sub>13</sub>]<sup>-</sup> the three bridging CO ligands lie in each of the three CoRu<sub>3</sub> planes in the propellor type arrangement,<sup>16</sup> diagram a. However to accommodate



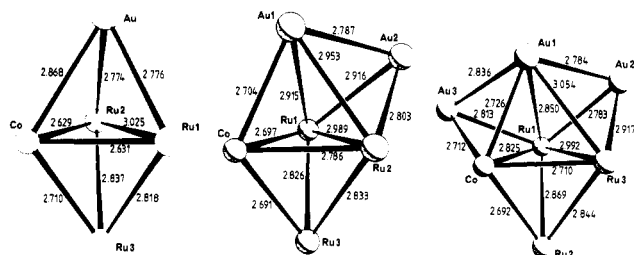
the Au atom one of these has swung around so that in 1 two of the bridging CO groups lie approximately in the equatorial Ru<sub>2</sub>Co plane, diagram b. There has been a concomitant twisting of the other bridging and terminal carbonyl groups to give a less staggered arrangement than in the precursor anion. In particular the two equatorial carbonyls C(11)-O(11) and C(22)-O(22) are eclipsed across the Ru(1)-Ru(2) bond which may account for the unusually long separation noted above.

It is interesting that the Au has capped a CoRu<sub>2</sub> face of the anion. In the corresponding hydride the H ligand was assumed on NMR evidence to cap the Ru<sub>3</sub> face.<sup>16</sup> However, the difference probably arises from the crowding on the Ru<sub>3</sub> face associated with the three terminal carbonyls on each Ru, the Ru<sub>2</sub>Co face being less sterically congested. Significantly, in other systems where an incoming Au atom can only add to a similar Ru<sub>3</sub> face a  $\mu$ -edge-bridging, rather than a  $\mu_3$ -face-bridging, site is found.<sup>4,8b,10,11a,15</sup>

Overall electron counting shows that 1 is a 72 electron cluster with  $(n + 1)$  skeletal pairs, according to the Wade method.<sup>22</sup> The observed closo trigonal-bipyramid core is therefore that expected. Localized electron counts at each metal give 18 electrons at Ru(3) and Co but 19 electrons for Ru(1) and Ru(2); the electron-rich nature of these latter atoms may contribute to the long distance between them.

**The Structure of (Ph<sub>3</sub>PAu)<sub>2</sub>CoRu<sub>3</sub>(H)(CO)<sub>12</sub>.** Molecules of 2 are formally derived from 1 by the replacement of one CO group by AuPPh<sub>3</sub> and H ligands. The AuPPh<sub>3</sub> moiety caps an AuRu<sub>2</sub> face to give a capped trigonal-bipyramidal cluster core, reminiscent of those found for Os<sub>6</sub>(CO)<sub>18</sub> and (Ph<sub>3</sub>PAu)<sub>2</sub>Os<sub>4</sub>H<sub>2</sub>(CO)<sub>12</sub><sup>5a</sup> which are also 84 valence electron clusters. Each of the three Ru atoms has three terminal CO ligands while the Co has three distinct types of CO associated with it. One [C(43)-O(43)] is purely terminal and one [C(42)-O(42)] unsymmetrically bridges the Co-Ru(3) bond (Co-C = 1.74 Å, Ru-C = 2.23 Å) while the third is semibridging toward Ru(1) [Co-C = 1.68 Å, Ru-C = 2.49 Å]. The H ligand was not located in the X-ray determination but is required to explain the diamagnetism of 2 and confirmed by <sup>1</sup>H NMR. Space-filling diagrams indicate a hole along the Co-Ru(2) bond, suggesting that the hydride occupies a  $\mu$  position on this bond. This would explain why the Co-Ru(1) bond is semibridged by a CO ligand, whereas the Co-Ru(2) bond is not.

There are 12 distinct metal-metal bonds in 2. Comparing equivalent bonds in 1 and 2 the effect of adding the second AuPPh<sub>3</sub> cap is to (i) increase the Au(1)-Ru(1) and Au(1)-Ru(2) bonds by ca. 0.16 Å, (ii) decrease the Au(1)-Co distance by 0.16 Å, and (iii) increase the Co-Ru(1) and Co-Ru(2) distances, possibly by displacing the



**Figure 5.** Diagrams of the metal cores of the clusters, showing metal-metal bond lengths: (a) 1, (b) 2, and (c) 3.

bridging carbonyl ligands found along these bonds in 1. The Au-Au bond, 2.787 Å, is typical of those found in similar polygold clusters.

**The Structure of (Ph<sub>3</sub>PAu)<sub>3</sub>CoRu<sub>3</sub>(CO)<sub>12</sub> (3).** Details have been published separately,<sup>14</sup> but the main points are emphasised here for completeness. The structure is formally derived from 2 by addition of a Ph<sub>3</sub>PAu group and loss of the hydride ligand. The incoming gold atom has added to one of the two Au-Co-Ru faces of 2 to give a bicapped trigonal-bipyramidal Au<sub>3</sub>CoRu<sub>3</sub> core, similar to the Au<sub>3</sub>Ru<sub>4</sub> skeleton in (Ph<sub>3</sub>PAu)<sub>3</sub>Ru<sub>4</sub>(H)(CO)<sub>12</sub>.<sup>15</sup> The disposition of the CO ligands is little changed on going from 2 → 3 except that the semibridging CO of 2 becomes a fully bridging ligand in 3. Similarly there are only small changes in comparable bond lengths in 2 and 3.

## Discussion

The most interesting aspect of the structures reported herein is the geometry of the cluster cores (Figure 5). Starting from the anion [CoRu<sub>3</sub>(CO)<sub>13</sub>]<sup>-</sup> the first gold atom adds to one of the CoRu<sub>2</sub> faces, which are less hindered than the Ru<sub>3</sub> face. The second gold atom then adds to the AuRu<sub>2</sub> face of 1 which seems to be the least hindered face adjacent to the first gold atom. Finally, the third gold atom adds to one of the two equivalent Au-Co-Ru faces where a new Au-Au bond can form—the alternative sites on Au<sub>2</sub>Ru faces of 2 appear to be blocked by upward pointing CO ligands on Ru (Figure 4). The principle that governs the buildup of the clusters is apparently that successive gold atoms add to the least hindered triangular faces next to existing Au atoms; this leads to a compact structure consisting of face-sharing tetrahedra with as many adjacent gold atoms as possible. This pattern seems general for most polygold mixed-metal clusters reported to date although there are exceptions.<sup>5d</sup> There is also some theoretical basis for this pattern. Evans and Mingos<sup>23</sup> have examined the bonding tendencies of Au(PR<sub>3</sub>) fragments and have shown that these groups have a single sp-hybridized orbital suitable for bonding (which makes them isolobal with CH<sub>3</sub>, Co(CO)<sub>4</sub>, H, etc.) and also have two higher energy *p* orbitals which can make a lesser but still significant contribution to bonding. These interactions are particularly effective in condensed polyhedral structures based on tetrahedra.

Several reports have recently stressed the isolobal nature of Au(PR<sub>3</sub>) and H groups, and it has been suggested that gold derivatives of clusters may be used to predict H bonding sites when the corresponding hydride cannot be located directly. However our results show that this approach is not valid when more than one Au group is present; for example, the H ligands in the hydride analogue of 3, H<sub>3</sub>CoRu<sub>3</sub>(CO)<sub>12</sub>, are found in  $\mu$  positions along each Ru-Ru bond in the solid state.<sup>24</sup> Even when only one

(22) Wade, K. *Adv. Inorg. Chem. Radiochem.* 1976, 18, 1. Mingos, D. M. P.; Forsyth, M. *J. Chem. Soc., Dalton Trans.* 1977, 610.

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

Au(PR<sub>3</sub>) group is present the analogy does not always hold. For **1** the Au atom is on a CoRu<sub>2</sub> face whereas the H ligand of HCoRu<sub>3</sub>(CO)<sub>13</sub> is assigned to the Ru<sub>3</sub> face.<sup>16</sup> A similar discrepancy has recently been noted for the ( $\mu$ -X)Fe<sub>3</sub>(CO)<sub>9</sub>(HC=N-*t*-Bu) pair, X = H or Au(PPh<sub>3</sub>).<sup>25</sup>

Although the polytetrahedral structures found for **1**–**3** are very compact, with high connectivities, they are not fragments of close-packed structures. For *N* rigid spheres packing together under Lennard–Jones forces only, Hoare and Pal<sup>26</sup> have demonstrated that the minimum energy configurations for *N* = 5, 6, and 7 are the trigonal bipyramid, the octahedron, and the pentagonal bipyramid, respectively. However, the core structures observed for **2** and **3** are only 3.2% and 5.5% higher in energy than the corresponding minimum geometries and of course the presence of ligands casts some doubts on the relevance of the bare cluster calculations.

The core geometries of **1**–**3** are those predicted by the Wade–Mingos rules.<sup>22</sup> Implicit in this procedure is that capped structures have the same number of electron pairs for skeletal bonding as the parent closo cluster, which is six for each of **1**–**3**. Since the number of M–M bonds increases from nine in **1** to 15 in **3**, we might expect a decrease in bond order and hence an increase in bond lengths with increasing nuclearity. This is indeed observed although the changes are relatively minor; thus the average over all nine M–M bonds in **1** is 2.785 Å while the averages of the corresponding nine bonds of **2** and **3** are 2.821 and 2.840 Å, respectively.

Extensive calculations have recently been carried out on the electronic requirements of a large number of close-packed cluster geometries, using Rh as a "typical" metal atom.<sup>27</sup> These have shown that for clusters which

are fragments of close-packed lattices maximum stability is achieved if there are (6*N* + 7) cluster valence molecular orbitals (CVMO's) where *N* is the nuclearity of the cluster. Open structures have more than this number while clusters based on condensed face-sharing tetrahedra are characterized by (6*N* + 6) CVMO's.

Each of **1**, **2**, and **3** belongs to this last class and has the predicted (6*N* + 6) CVMO's [assuming CVMO's =  $\frac{1}{2}$ (number of valence electrons)], showing that the principles derived for Rh can be extended to mixed-metal clusters containing Au, although homometallic Au<sub>*n*</sub> type clusters are usually formally electron deficient.

### Conclusion

The [(Ph<sub>3</sub>PAu)<sub>3</sub>O]<sup>+</sup> cation has a useful application as an aurating agent in cluster synthesis since it can replace one CO ligand by two Ph<sub>3</sub>PAu groups, as well as acting as a source of Ph<sub>3</sub>PAu<sup>+</sup>. It therefore has an advantage over Ph<sub>3</sub>PAuCl or Ph<sub>3</sub>PAuMe, where the number of incoming gold atoms is limited to the number of negative charges or hydride ligands, respectively, on the cluster precursor. A wide range of higher nuclearity clusters can be synthesized via the route described herein starting from HCoRu<sub>3</sub>(CO)<sub>13</sub> or the corresponding anion. A number of other systems are currently being investigated to confirm the wide applicability of the method.

**Acknowledgment.** We thank the Australian Research Grant Committee for financial support and the University of Waikato for granting of study leave to B.K.N. We also thank Dr. M. R. Snow for use of X-ray facilities and for assistance with crystallography.

**Supplementary Material Available:** Tables of thermal parameters and structure factor amplitudes for **1** and **2** (38 pages). Ordering information is given on any current masthead page.

(24) Gladfelter, W. L.; Geoffroy, G. L.; Calabrese, J. C. *Inorg. Chem.* **1980**, *19*, 2569.

(25) Bruce, M. I.; Nicholson, B. K. *J. Organomet. Chem.* **1983**, *250*, 633.

(26) Hoare, M. R.; Pal, P. *Adv. Phys.* **1970**, *20*, 161.

(27) (a) Lauher, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 5305. (b) Lauher, J. W. *Ibid.* **1979**, *101*, 2604. (c) Lauher, J. W. *J. Organomet. Chem.* **1981**, *213*, 25. (d) Ciani, G.; Sironi, A. *Ibid.* **1980**, *197*, 233.