

Cluster Chemistry. Application of Gold–Oxonium Reagents to the Synthesis of Poly-gold Mixed-metal Clusters: Preparation and X-Ray Crystal Structure of $[\text{Au}_3\text{CoRu}_3(\text{CO})_{12}(\text{PPh}_3)_3]$, containing a Bicapped Trigonal-bipyramidal Metal Cluster

Michael I. Bruce and Brian K. Nicholson

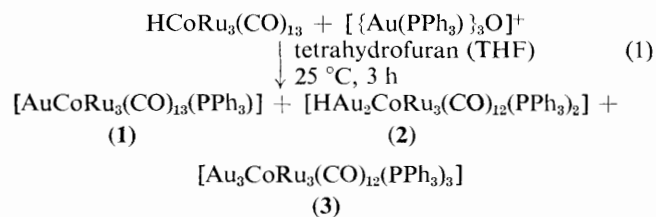
Jordan Laboratories, Department of Physical and Inorganic Chemistry, University of Adelaide, South Australia, 5000

Reaction between $[\{\text{Au}(\text{PPh}_3)_3\}\text{O}] [\text{BF}_4]$ and $[\text{HCoRu}_3(\text{CO})_{13}]$ or $[\text{CoRu}_3(\text{CO})_{13}]^-$ gives good yields of the title cluster which has been shown by an X-ray crystal structure analysis to have a seven-metal-atom skeleton, in which two gold atoms cap adjacent AuCoRu and AuRu₂ faces of the trigonal bipyramidal AuCoRu₃ core.

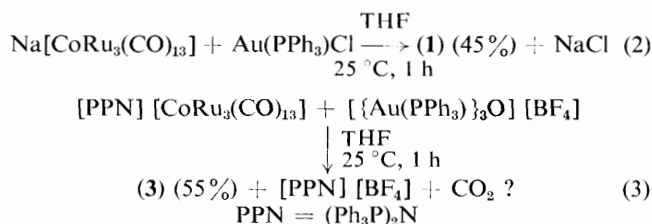
There have been several recent reports of mixed metal clusters incorporating gold atoms in the framework.^{1,2} Preparative routes include reactions between metal cluster anions and $[\text{AuCl}(\text{PR}_3)]$ or $[\text{Au}(\text{PR}_3)_2]^+$, and oxidative addition of $[\text{AuX}(\text{PR}_3)]$ to suitable neutral clusters. In the majority of examples where structures are known the gold atom enters an edge-bridging position, although in $[\text{AuCo}_3\text{Fe}(\text{CO})_{12}(\text{PPh}_3)]$ the gold caps a Co₃ face of the FeCo₃ tetrahedron to give a trigonal bipyramid of metal atoms. These observations support the proposal that the Au(PR₃) moiety tends to become attached to cluster anions in the positions occupied by the H-ligands in the corresponding hydrides.²

We draw attention to the use of $[\{\text{Au}(\text{PPh}_3)_3\}\text{O}] [\text{BF}_4]$ which promises to have wide application in the syntheses of mixed metal clusters since it can introduce up to three gold atoms to a cluster simultaneously. (This reagent has been used previously³ to aurate organic precursors. The addition of three Au(PPh₃) groups to $[\text{V}(\text{CO})_5]^{3-}$ to give a VAu₃ cluster has also been described.¹)

Reaction between $[\text{HCoRu}_3(\text{CO})_{13}]^-$ and $[\{\text{Au}(\text{PPh}_3)_3\}\text{O}] [\text{BF}_4]$ gives products containing one, two, or three gold atoms, which are readily separated by preparative t.l.c. [equation (1)]. The actual course of the reaction is not clear; stepwise addition of Au(PR₃) moieties is ruled out by (i), the lack of reaction between (1) and excess of $[\{\text{Au}(\text{PPh}_3)_3\}\text{O}]^+$ and (ii), the formation of (1)–(3) together with unreacted $[\text{HCoRu}_3(\text{CO})_{13}]$ when a deficit of oxonium reagent is used. Alternar-



tive and more specific routes to (1) and (3) have also been developed, equations (2) and (3). The new species (1)–(3)



have been characterised by elemental analyses and i.r. spectroscopy,[†] while (1) and (3) have been subjected to full crystal structure determinations. Cluster (1) has a trigonal bipyramidal core with an Au(PPh₃) fragment capping the CoRu₂ face of the parent $[\text{CoRu}_3(\text{CO})_{13}]^-$ anion, and is thus similar to the previously reported³ $[\text{AuCo}_3\text{Fe}(\text{CO})_{12}(\text{PPh}_3)]$; the details are not reported here. The structure of (2) has yet to be determined but analytical and physical properties are consistent with the formula given in equation (1). The structure of (3) reveals a previously unknown seven-metal-atom core geometry.

Crystal Data: C₆₆H₄₅Au₃CoO₁₂P₃Ru₃, *M* = 2076, triclinic, space group $\overline{P}1$; *a* = 13.944(2), *b* = 14.105(3), *c* = 20.365(6) Å, α = 68.62(2), β = 79.16(2), γ = 63.89(2)°, *U* = 3347 Å³, *D_m* = 2.05, *D_c* = 2.06 g cm⁻³ for *Z* = 2, *F*(000) = 1956, λ(Mo-*K*_α) = 0.7107 Å, μ(Mo-*K*_α) = 75 cm⁻¹, *t* = 23 °C. The structure was solved by direct methods

[†] $[\text{AuCoRu}_3(\text{CO})_{13}(\text{PPh}_3)]$, (1): ν(CO) (CH₂Cl₂) 2086m, 2041vs, 1985br.m, 1899w, and 1848m cm⁻¹. $[\text{Au}_2\text{CoRu}_3(\text{H})(\text{CO})_{12}(\text{PPh}_3)_2]$, (2): ν(CO) 2069s, 2026vs, 2008sh.m, 1968m, and 1830br. w cm⁻¹; ¹H n.m.r. (CDCl₃), δ 7.36 (m, PPh₃) and -11.6 (br.s, hydride). $[\text{Au}_3\text{CoRu}_3(\text{CO})_{12}(\text{PPh}_3)_3]$, (3): ν(CO)(CH₂Cl₂) 2058s, 2014s, 2000s, 1984m, 1956m, 1840w, and 1810w cm⁻¹.

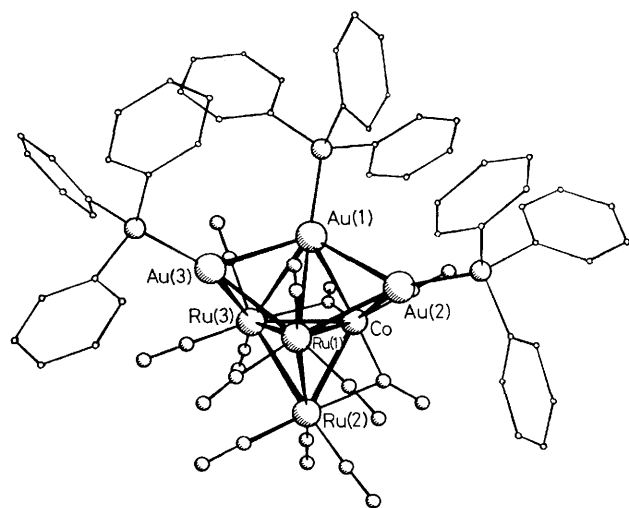
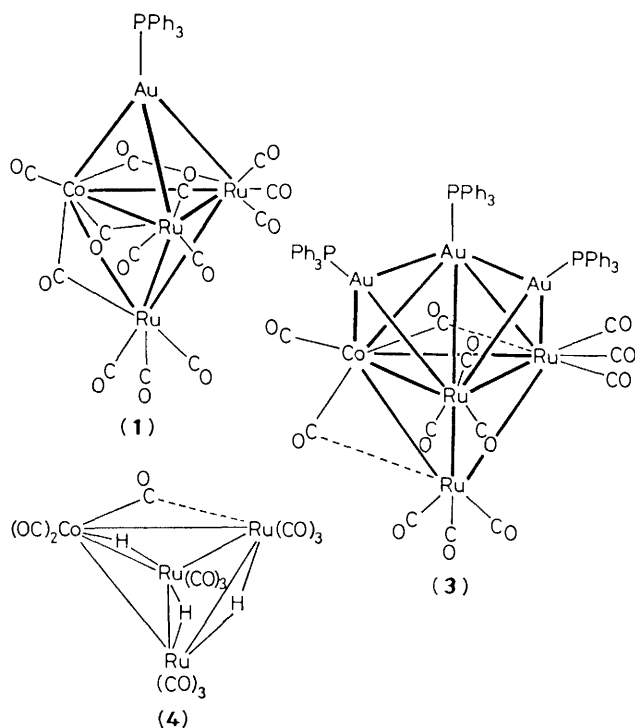


Figure 1. A molecule of complex (3).

and refined to $R = 0.053$, $R_w = 0.055$ for 3843 unique, absorption-corrected data for which $I \geq 2.5\sigma(I)$ and $3.0 \leq 2\theta \leq 40^\circ$. In the final cycle of refinement metal and phosphorus atoms were assigned anisotropic thermal parameters and the carbon and oxygen atoms were treated isotropically. Phenyl rings were included as rigid groups with the hydrogen atoms given calculated positions and a common temperature factor.† Figure 1 shows one molecule of complex (3). The polymetallic core is best described as bicapped trigonal bipyramidal (or, equivalently, as tricapped tetrahedral), with a trigonal bipyramid of AuCoRu₃ atoms (Au and Co in apical positions) and the two remaining Au atoms capping

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

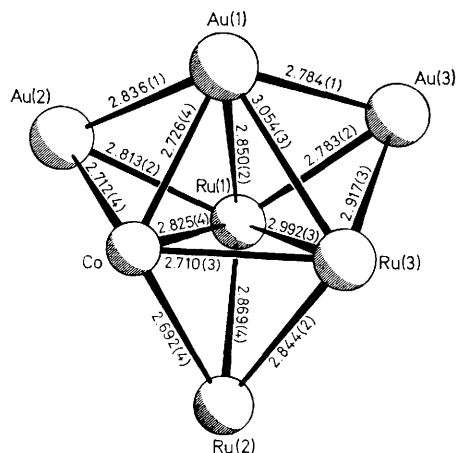


Figure 2. The Au₃CoRu₃ core of (3), showing metal-metal separations.

the AuCoRu and AuRu₂ faces. Each Au is also bonded to a PPh₃ ligand, while each of the other metal atoms is attached to three terminal CO groups, although two of those attached to cobalt are semi-bridging towards adjacent ruthenium atoms. There are fifteen formal metal-metal bonds varying in length from 2.692(4) to 3.054(3) Å; details are given in Figure 2.

The hydride analogous to (3) is [H₃CoRu₃(CO)₁₂] which exists as two isomers: in the C₁ isomer (4), the three hydrogen atoms bridge the Co-Ru and two Ru-Ru bonds.⁶ In this isomer also, a CO group semi-bridges a Co-Ru bond. Some similarities between (3) and (4) can be traced, but the chief difference is that the three gold atoms are within bonding distance of each other, and occupy face-capping, rather than edge-bridging positions. Indeed, the structure of (3) is obtained by formal addition of two Au(PPh₃) fragments to the AuCoRu and AuRu₂ faces of (1).

The wide variation in metal-metal bond lengths is best understood in terms of a delocalised bonding picture, rather than by using a simple two electron, two centre model as required by the H-AuPR₃ analogy. Electron counting shows that (3) is a 96-electron cluster. For a seven-atom cluster, Wade's rules predict a structure with six skeletal bonding electron pairs; the observed bicapped trigonal bipyramid core is therefore that predicted.⁷ This particular geometry has not been previously observed nor has it been considered in any of the several theoretical studies on cluster shapes.^{8,9} In fact the bicapped trigonal bipyramid arrangement is unusually compact. Lauher⁸ has used the ratio of cluster valence molecular orbitals (CVMO) to metal atoms (N) to quantify 'compactness.' The ratio $CVMO:N$ varies from 9.0:1 for a single atom to below 6 for bulk metals. If the 48 MO's are distributed over the seven metal atoms, the ratio for (3) is 6.86:1, significantly lower (*i.e.* more 'bulk-metal-like') than that found for alternative 7-atom geometries. Similar $CVMO:N$ ratios have been observed previously only for clusters with nuclearity >12 .§ This compactness in (3)

§ Although Lauher's determination of the number of CVMO is based on extended Hückel MO calculations on isolated Rh_n clusters, the results are reliable guides to cluster stoichiometries based on the usual cluster electron counts. While the specific geometry found for (3) was not considered, a related close-packed 7-atom structure (capped octahedron) was found to have 49 CVMO; since the number of CVMO increases as the cluster becomes more open, it is not unreasonable that there would be 48 CVMO in (3) to accommodate its 96 electrons. This matter will be explored in more detail in a full account to be published elsewhere.

gives rise to high connectivities; for example, Ru(1) is involved in six metal-metal bonds as well as three metal-ligand bonds giving it a particularly high formal co-ordination number.

A similar reaction between $[\{\text{Au}(\text{PPh}_3)_3\text{O}\} [\text{BF}_4]$ and $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ gives red $[\text{H}_3\text{AuRu}_4(\text{CO})_{12}(\text{PPh}_3)]$ and brown (green in benzene) $[\text{HAu}_3\text{Ru}_4(\text{CO})_{12}(\text{PPh}_3)_3]$, illustrating the generality of gold-oxonium reagents for introducing Au(PR₃) groups into clusters.

We thank the Australian Research Grants Committee for financial support, the University of Waikato for study leave (to B.K.N.), T. W. Hambley for assistance with crystallography, and Dr. M. R. Snow for use of X-ray facilities.

Received, 21st June 1982; Com. 716

References

- 1 J. Lewis and B. F. G. Johnson, *Pure Appl. Chem.*, 1982, **54**, 97 and references cited therein; B. F. G. Johnson, D. A. Kaner, J. Lewis, P. R. Raithby, and M. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 1982, 314; M. J. Mays, P. R. Raithby, P. L. Taylor, and K. Henrick, *J. Organomet. Chem.*, 1982, **224**, C45.
 - 2 J. W. Lauher and K. Wald, *J. Am. Chem. Soc.*, 1981, **103**, 7648.
 - 3 A. N. Nesmeyanov, E. G. Perevalova, Y. T. Struchkov, M. Y. Antipin, K. I. Grandberg, and V. P. Dyadchenko, *J. Organomet. Chem.*, 1980, **201**, 343.
 - 4 J. E. Ellis, *J. Am. Chem. Soc.*, 1981, **103**, 6106.
 - 5 P. C. Steinhardt, W. L. Gladfelter, A. D. Harley, J. R. Fox, and G. L. Geoffroy, *Inorg. Chem.*, 1980, **19**, 332.
 - 6 W. L. Gladfelter, G. L. Geoffroy, and J. C. Calabrese, *Inorg. Chem.*, 1980, **19**, 2569.
 - 7 B. F. G. Johnson and J. Lewis, *Adv. Inorg. Chem. Radiochem.*, 1981, **24**, 225; K. Wade, *ibid.*, 1976, **18**, 1.
 - 8 J. W. Lauher, *J. Organomet. Chem.*, 1981, **213**, 25; J. W. Lauher, *J. Am. Chem. Soc.*, 1979, **101**, 2604; J. W. Lauher, *J. Am. Chem. Soc.*, 1978, **100**, 5305.
 - 9 G. Ciani and A. Sironi, *J. Organomet. Chem.*, 1980, **197**, 233.
-