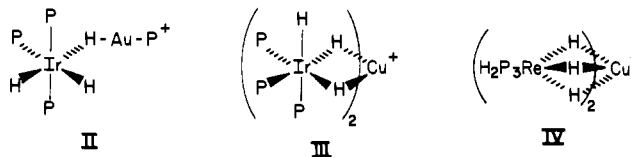


Figure 1. ORTEP views down (a) and nearly perpendicular to (b) the crystallographic C_3 symmetry axis of $\text{Ir}_2\text{Cu}_3\text{H}_6(\text{NCMe})_3(\text{PMe}_2\text{Ph})_6^{3+}$. Only the metals and the inner coordination sphere are shown (i.e., P, acetonitrile N, and hydride). The hydride positions have been added to the heavy atom structure determined by X-ray data by assuming colinearity with the Ir-P vectors and using an Ir-(μ -H) distance of 1.75.¹³ This gives a Cu-(μ -H) distance of 1.91 Å. Selected structural parameters: Cu-Ir, 2.793 (9); Cu-Cu, 2.570 (22); Ir-P, 2.347 (6) Å; \angle P-Ir-P, 101.7 (2)°.

formula $[\text{Ir}_2\text{Cu}_3\text{H}_6(\text{MeCN})_3(\text{PMe}_2\text{Ph})_6](\text{PF}_6)_3$. The metal atoms adopt a trigonal bipyramidal form (Figure 1), with iridium axial and a facial array of three phosphines on each iridium. Each copper is bonded to one acetonitrile. Unlike trigonal bipyramidal^{6,7} $\text{Cu}_5(\mu_2\text{-Ph})_6^-$ and $\text{Cu}_5(\mu_2\text{-S-}i\text{-Bu})_6^-$, both of which have nonbonded Cu...Cu distances of >3.1 Å between the (equatorial) coppers, the copper-copper separation in $\text{Ir}_2\text{Cu}_3\text{H}_6(\text{MeCN})_3(\text{PMe}_2\text{Ph})_6^{3+}$ is bonding (2.57 (2) Å). Although hydride atoms were not located by using the diffraction data, they can be confidently placed in positions trans to the Ir-P vectors on the basis of the AA'A''XX'X'' patterns in the ^1H and ^{31}P NMR spectra.⁸ Curiously, this puts them neither precisely over the Cu-Ir lines nor symmetrically over the Cu_2Ir triangular faces (Figure 1a).

Each metal center in the observed structure achieves an 18 valence electron count if $\text{Ir}_2\text{Cu}_3\text{H}_6(\text{MeCN})_3(\text{PMe}_2\text{Ph})_6^{3+}$ is dissected into 6H^+ and $\text{Ir}_2\text{Cu}_3(\text{MeCN})_3(\text{PMe}_2\text{Ph})_6^{3-}$ in order to eliminate the question of how to count μ -hydrides. Every metal-metal edge must be considered as being a single bond in the 3-ion, and the actual ion is then reconstituted by protonating all six Ir-Cu bonds.⁹ In this same formalism, $\text{CuIr}_2\text{H}_6(\text{PMe}_2\text{Ph})_6^+$ has two Ir=Cu double bonds, each of which is doubly protonated (see I). Consistent with this, the Ir-Cu separation in $\text{CuIr}_2\text{H}_6(\text{PMe}_2\text{Ph})_6^+$ (2.51 Å) is 0.28 Å shorter than that in the Ir_2Cu_3 cation reported here (2.79 Å).

The structural chemistry developed thus far between group 11 cations and metal polyhydrides shows a persuasive analogy between the polyhydride unit and coordinated BH_4^- , II,¹⁰ III, and IV corresponding to η^1 -, η^2 -, and η^3 - BH_4^- . In $\text{Ir}_2\text{Cu}_3\text{H}_6(\text{MeCN})_3(\text{PMe}_2\text{Ph})_6^{3+}$ we have an analogue of μ, η^3 - BH_4^- found in $\text{Fe}_2\text{H}(\text{BH}_4)(\text{CO})_9$.¹¹ This analogy works in both directions, suggesting



$\text{Cu}_3(\text{NCMe})_3(\mu, \eta^3\text{-BH}_4)_2^+$ as a plausible synthetic target. Finally, an accompanying paper shows how three H_3RhP_3 units may bridge all edges of an Ag_3^{3+} triangle in a μ_2, η^3 fashion, analogous to the bridging borohydride in $\{\text{CoBH}_4[\text{Ph}_2\text{P}(\text{CH}_2)_5\text{PPh}_2]\}_2$.¹²

Acknowledgment. We thank NSF (CHE-8305281) for financial support, Johnson, Matthey Co. for loan of chemicals, and Professor L. Venanzi for discussion of his results prior to publication.

Registry No. *fac*- IrH_3P_3 , 12099-83-1; $\text{Cu}(\text{NCMe})_4\text{PF}_6$, 64443-05-6; $[\text{Ir}_2\text{Cu}_3\text{H}_6(\text{MeCN})_3(\text{PMe}_2\text{Ph})_6](\text{PF}_6)_3$, 95018-01-2; Cu, 7440-50-8; Ir, 7439-88-5.

Supplementary Material Available: Listing of atom coordinates, bond lengths, and bond angles for $[\text{Cu}_3(\text{NCMe})_3[\text{IrH}_3(\text{PMe}_2\text{Ph})_3]_2](\text{PF}_6)_3$ (2 pages). Ordering information is given on any current masthead page.

(11) Vites, J. C.; Eigenbrot, C.; Fehlner, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4633.

(12) Holah, D. G.; Hughes, A. N.; Maciaszek, S.; Magnuson, V. R. *J. Chem. Soc., Chem. Commun.* **1983**, 1308.

(13) Bau, R.; Carroll, W. E.; Hart, D. W.; Teller, R. G.; Koetzle, T. F. *Adv. Chem. Ser.* **1978**, No. 167, 71.

Formation of a Planar Hexametallc Cluster Containing a Triangle of Silver Atoms within a Triangle of Rhodium Atoms

Fiorella Bachechi

*Istituto di Strutturistica Chimica
"Giordano Giacomello", CNR, C.P.N. 10
I-00016 Monterotondo Stazione, Roma, Italy*

Jurg Ott and Luigi M. Venanzi*

*Laboratorium für Anorganische Chemie, ETH Zentrum
CH-8092 Zürich, Switzerland*

Received October 16, 1984

One of the most recurrent features of transition-metal cluster chemistry is the presence of triangular metal units.¹ Such units have also been found in cluster compounds of the coinage metals and of gold in particular.² It has also been observed that these "building blocks" frequently contained one or more hydrogen atoms in bridging positions between two or more metal atoms.³ Furthermore, tripodlike ligands facilitate both cluster⁴ and hydrogen-bridge⁵ formation. Thus, attempts to obtain mononuclear hydrido complexes of elements of the first transition series containing the ligand $\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$ (tripod) resulted in the formation of the binuclear compounds $[(\text{tripod})\text{M}(\mu\text{-H})_3\text{M}(\text{tripod})]^+$ (M = Fe and Co).⁶

(1) Muetterties, E. L. *J. Organomet. Chem.* **1980**, *200*, 177 and references cited therein.

(2) Evans, D. G.; Mingos, D. M. P. *Organometallics* **1983**, *2*, 435 and references cited therein.

(3) For a review of compounds of this type, see: *Adv. Chem. Ser.* **1978**, No. 167, 1-121.

(4) Ceconi, F.; Ghilardi, C. A.; Midollini, S.; Orlandini, A. *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 554.

(5) Sacconi, L.; Mani, F. *Transition Met. Chem. (Weinheim, Ger.)* **1982**, *8*, 179.

(6) (a) Dapporto, P.; Fallani, G.; Midollini, S.; Sacconi, L. *J. Am. Chem. Soc.* **1973**, *95*, 2021. (b) Dapporto, P.; Midollini, S.; Sacconi, L. *Inorg. Chem.* **1975**, *14*, 1643.

(6) Edwards, P. G.; Gellert, R. W.; Marks, M. W.; Bau, R. *J. Am. Chem. Soc.* **1982**, *104*, 2072.

(7) Bowmaker, G. A.; Clark, G. R.; Seadon, J. K. *Polyhedron* **1984**, *3*, 535.

(8) The poor definition of the fine structure in the hydride resonance is attributed to broadening by quadrupolar copper.

(9) Implicit in this formalism is an 18-electron count at copper. This explains the unusual result that the Ir_2Cu_3 cation is the first product found to incorporate coordinated acetonitrile.

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

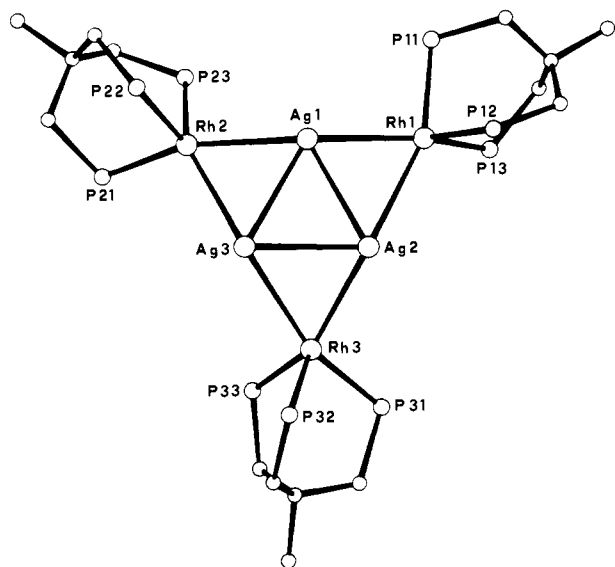


Figure 1. A perspective drawing of the cation $[\text{Rh}_3\text{Ag}_3\text{H}_9(\text{tripod})_3]^{3+}$ (**2**). The terminal phenyl groups have been omitted for clarity. The hydride positions are not indicated as they could not be determined.

During the course of our studies of the reactivity of $[\text{RhCl}_3(\text{tripod})]^{3+}$ (**1**) we found that when a methanolic solution of **1** was treated with 4 equiv of AgCF_3SO_3 , the precipitated AgCl filtered off, and dihydrogen bubbled through the solution, crystals of the apparent composition " $\text{RhAgH}_3(\text{CF}_3\text{SO}_3)(\text{tripod})$ "⁸ were obtained.

The X-ray crystal structure⁹ of this compound shows that it contains the cation $[\text{Rh}_3\text{Ag}_3\text{H}_9(\text{tripod})_3]^{3+}$ (**2**) associated with CF_3SO_3^- anions. A perspective view of the heavy atoms of **2** is shown in Figure 1. As can be seen, the silver atoms form an equilateral triangle¹⁰ centered within an equilateral triangle of rhodium atoms. The six metal atoms are practically coplanar. This structure can be considered as resulting from the interaction of one monomeric *fac*- $[\text{RhH}_3(\text{tripod})]$ complex,¹¹ **3**, with each Ag–Ag edge. All the Rh–Ag contacts are hydrogen bridged and there is an alternation of single and double bridges around the Rh triangle. This structure is suggested by the relative positions of the rhodium and phosphorus atoms. Thus, if one considers the coordination geometry around Rh(1) one notices that Rh(1), Ag(1), Ag(2), Ag(3), and P(11) are coplanar and that this plane bisects the P(12)–Rh(1)–P(13) angle. Thus, given the approximate octahedral coordination of the donor atoms of **3**, one can assume that the hydride ligands in trans positions to P(12) and to P(13) are situated between Rh(1) and Ag(1) respectively below and above the plane of the metal atoms. Similarly, one can postulate that the hydride ligand in trans position to P(11) is located between Rh(1) and Ag(2), forming the usual bent M–H–M bridge.³ A similar description applies to Rh(2) and Rh(3).

(7) Siegl, W. O.; Lapporte, S. J.; Collman, J. P. *Inorg. Chem.* **1971**, *10*, 2158.

(8) Analytical determination by X-ray fluorescence of the Rh:Ag:S:P ratio gave the values 1:1.14:1.08:2.96 and NMR integration of the CH_3 protons of tripod relative to the sum of the resonances in the hydride region gave the ratio 1:1.

(9) Crystallographic data (room temperature): monoclinic space group $P2_1/n$ with $a = 29.007$ (6) Å, $b = 16.786$ (5) Å, $c = 27.095$ (6) Å, $\beta = 90.87$ (3)°, $V = 13192$ Å³, and $Z = 4$. 7850 reflections corrected for decay and absorption, with an $I > 3\sigma(I)$, were used for the least-square refinement which, at the present stage, gives the value $R = 0.120$. Although the exact positions of the anions have not been unambiguously located, there are no significant electron density peaks in the neighborhood of the silver atoms, indicating that the complete coordination environment of the Ag atom is that indicated in Figure 1.

(10) The Ag–Ag distance (2.968 (4)–2.998 (4) Å) are longer to those found in metallic Ag (2.8894 Å). See: "CRC Handbook of Chemistry and Physics", 61st ed.; Chemical Rubber Publishing Co.: Cleveland, 1980; p F 219.

(11) This mononuclear complex has been directly prepared and its X-ray crystal structure determined. Ghilardi, C. A.; Midollini, S.; Orlandini, A.; Ott, J.; Venanzi, L. M., unpublished results.

This structural assignment is supported by the alternation of the Rh–Ag distances, which shows shorter contacts (2.795 (4)–2.807 (4) Å) where a double hydrogen bridge has been postulated and longer contacts (2.884 (4)–2.933 (4) Å) for the others.

Further support for this formulation comes from the IR spectrum of **2**, which shows no IR band in the region 1800–2200 cm^{-1} , while one observes a broad absorption band centered at 1630 cm^{-1} ,¹² indicating that all nine hydride ligands are bridging.

The ^1H and ^{31}P NMR spectra¹³ of compound **2** at room temperature give fairly broad resonances which sharpen below ca. -15 °C. Analysis of the resulting multiplets for both nuclei¹⁴ at -20 °C shows that each "RhH₃(tripod)" unit is coupled to two silver atoms. The hydrides and the phosphorus atoms remain chemically equivalent down to ca. -80 °C where line broadening sets in again. Thus, in the temperature range -80 to -20 °C, each RhH₃(tripod) unit, although localized on an Ag–Ag edge, can be considered as fluxional with respect to the microgeometry at a single rhodium.

Two reactivity patterns of cluster **2** are worthy of note: (a) while it is stable in acid solution, e.g., in 1 M methanolic $\text{CF}_3\text{SO}_3\text{H}$, in neutral or basic solution it slowly decomposes with formation of metallic silver (it is likely that, because of its high charge, cation **2** can easily deprotonate and that the resulting rhodium(I) species undergoes an H–Ag charge-transfer process); (b) no precipitation of AgCl occurs on addition of chloride to a methanolic solution of **2** (the ^{31}P NMR spectrum of this solution shows the presence of a new complex, which can also be obtained by adding AgCl to a CH_2Cl_2 solution of **3**).

Cluster **2** is obviously related to the iridium–copper cluster $[\text{Ir}_2\text{Cu}_3\text{H}_6(\text{MeCN})_3(\text{PMe}_2\text{Ph})_3]^{3+}$ (**4**), described by Rhodes et al.¹⁵ Its central unit is constituted by a triangle of copper atoms, which in **4** is capped on each side by a *fac*- $[\text{IrH}_3(\text{PMe}_2\text{Ph})_3]$ unit. Furthermore, the formally copper(I) metal centers can be considered as *three-coordinate*, i.e., bonded to two hydrogen atoms and to the nitrogen atom of acetonitrile. Both features, *mutatis mutandis*, are retained in our cluster where the central triangle is made up of silver(I) atoms and each of them is three-coordinate, the donor atoms being hydrogen atoms as no other potential donor atom is located near this metal center.⁹

Finally, it should be noted that transition-metal polyhydrides can form a wide range of heterometallic complexes containing coinage metals.¹⁶ This tendency appears to be particularly marked for compound **3** and its iridium analogue¹⁷ which give heterometallic compounds with bridging hydrides containing copper, silver, or gold depending on (a) the reaction conditions and/or (b) the ratio of reagents. Their full characterization is in progress. Thus compounds **2** and **4** appear to represent first examples of a new and extensive class of compounds of great potential significance for pure and applied chemistry.

Acknowledgment. We thank the Swiss National Science Foundation for financial support and Professor K. G. Caulton for discussion of his results prior to publication.

Registry No. **1**, 62792-06-7; **2**, 94978-18-4; Rh, 7440-16-6.

Supplementary Material Available: Listing of atom coordinates, bond lengths, and bond angles for **2** and a schematic drawing showing all the non-hydrogen atoms of cation **2** (8 pages). Ordering information is given on any current masthead page.

(12) The IR spectra were recorded in KBr disks. (The $\nu(\text{Rh-H})$ bands in **3** appear as a strong, not very sharp peak centered at 1900 cm^{-1} .)

(13) Measured in CD_2Cl_2 solutions with a Bruker WM 250 spectrometer.

(14) ^1H NMR (-20 °C) δ (hydride) -7.6 (d × d × t, $^2J(\text{P,H}) = 93$ Hz, presumably PH trans, $J(\text{Rh,H}) = 8.5$, $J(\text{Ag,H}) = 44$ Hz, presumably a sum of couplings), ^{31}P NMR (-20 °C) δ 19.5 (d × t, $J(\text{Rh,P}) = 94$, $J(\text{Ag,P}) = 21$ Hz).

(15) Rhodes, L. F.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.*, preceding paper in this issue.

(16) (a) Rhodes, L. F.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.*, preceding paper in this issue. (b) Connelly, N. G.; Howard, J. A. K.; Spencer, J. L.; Woodley, P. K. *J. Chem. Soc., Dalton Trans.* **1984**, 2003.

(17) (a) Ott, J., unpublished results. (b) Janser, P. Diplomarbeit, ETH, 1984.