

Low Nuclearity Gold Clusters, Structure and Bonding

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The area of metal cluster chemistry holds interest for many reasons. First, clusters provide an observable surface for the study of catalytic processes, sometimes with different activity than the bulk metal. Second, understanding the bonding within clusters offers a challenge to chemists. Finally, clusters of large size are may also be regarded as an intermediate state of matter between molecular and bulk. The study of such systems can help determine the point at which metallic behavior is first observed as metal clusters grow in size.

Gold clusters hold special interest within the realm of metal cluster chemistry. In terms of applications, gold clusters are being investigated as novel materials for electronics and nonlinear optics [1], and are used as labeling agents in biochemistry [2]. Recent work has also shown low nuclearity gold clusters catalyzing the decomposition of N_2O [3]. Investigation of gold clusters using ^{197}Au Mossbauer spectroscopy and other techniques will hopefully define the transition from a molecular cluster of metal atoms to a nanoparticle with metallic characteristics [1,4]. Work on gold clusters bonded to bridging ligands may improve our understanding of the bonding of atoms to metallic surfaces.

A knowledge of the lower nuclearity clusters (3-13 gold atoms) is essential to understand the activity and explain the structures of clusters such as Au_{55} and larger. A notable feature of the bonding of gold has been identified, which is the unusually large attraction between gold atoms, even with both gold atoms having a d^{10} configuration. The term "aurophilicity" was coined to describe this [5]. Aurophilicity has been suggested to contribute to the ability of $\text{Au}(\text{PPh}_3)$ fragments to induce hyperconjugation around first and second row main group atoms [6], as well as to contribute to the stabilization of clusters. In crystals of gold compounds, the aurophilic attraction affects the orientations of the molecules to maximize gold-gold contacts. Estimates for the bond strength vary from 25 to 46 kJ/mol, and the nature of the ligands on the gold atoms appear to alter the aurophilic interaction strength [11]. An example of this is the twisting chain of chloro(trimethylphosphine)gold in crystalline form (Figure 1). The origin of aurophilicity has been actively investigated since its inception. It is generally understood that relativistic effects in the gold atoms cause the contraction and subsequent lowering in energy of the 6s and to a lesser extent the 6p orbitals. This causes a greater screening of the 5d electrons from the nucleus by the 6s, expanding the 5d orbital and raising its energy. The lanthanide contraction also serves to bring these two orbitals closer in energy. The relative energy levels of the 6s, 6p, and 5d orbitals are shown before and after these two effects (Figure 2). The consequence of the narrow gap in energy

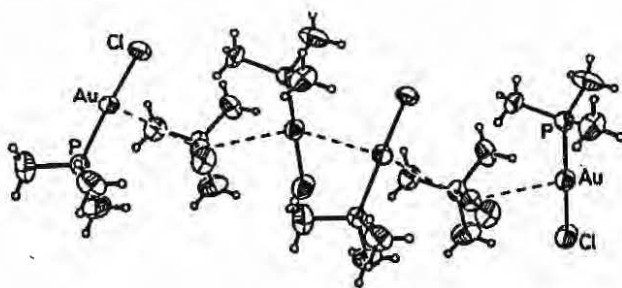


Figure 1

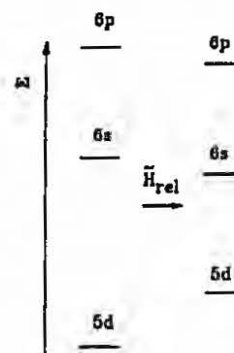


Figure 2

levels between these orbitals is the mixing of 5d with 6s and 6p orbital character, though contribution from the 6p orbital is small [8]. The relativistic effects just described cause the properties of gold to diverge from periodic trends. The cluster chemistry is also much different than that of copper or silver, which are not affected to the same degree by relativistic effects.

Illustration of the unique cluster-forming properties of gold are the "toroidal" clusters formed as AuPPh₃ units aggregate around a central gold atom in a belt, with additional AuPPh₃ units in some cases bonding to a triangular face of the belt rather than to the central atom [9]. "Spherical" clusters form with peripheral groups distributed around the surface of a sphere centered by a gold atom. The toroidal clusters have electron counts of $12n + 16$, while the spherical cluster has an electron count of $12n + 18$, where n is the number of perimeter AuPPh₃ groups. The toroidal belt may be hexagonal or octagonal, with the octagonal belt resembling a crown, such as [Au{P(p-C₆H₄OMe)₃}₈](BF₄)₃ (Figure 3). The octagonal belt apparently has a soft potential energy surface between the crown structure (D_{4h}) and a the structure (D_{2h}) of [Au₉{P(p-C₆H₄Me)₃}₈](PF₆)₃ that resembles a hexagonal ring with two extra gold atoms on directly opposite sides (Figure 4). These two configurations are adopted because of a slight change in ligand.

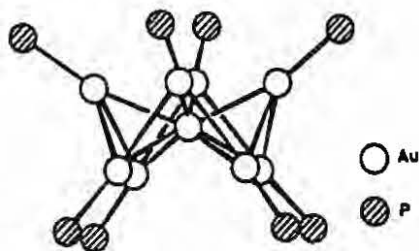


Figure 3

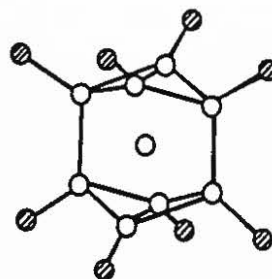


Figure 4

The polyhedral skeletal electron count provides one approach for the prediction of some gold cluster geometries, but a molecular orbital approach can also be enlightening to understand lower nuclearity clusters (3-6 gold atoms). For instance, to understand why Au₆(PH₃)₆ forms a pair of tetrahedra joined at the edge rather than an octahedral cluster, the molecular orbitals participating in the cluster bonding must be examined. The stabilization of such a cluster is due to the lowering in energy of the bonding molecular orbitals of the shared-edge tetrahedra versus

those of the octahedral cluster. While electron counting or molecular orbital approaches can provide insight to the homometallic clusters, clusters centered with p-block elements are most easily explained with the isolobal analogy which follows.

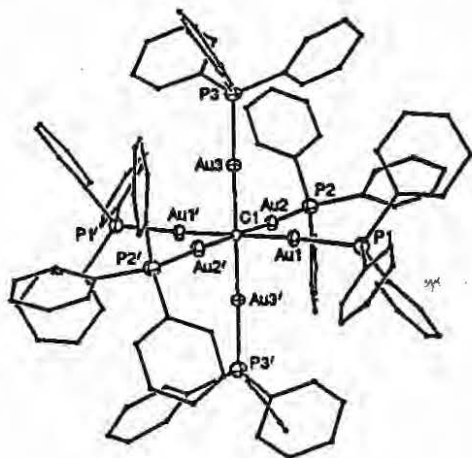


Figure 5

The assembly of Au(PPh₃) units around main-group elements has attracted interest not only because of the interesting hypercoordination observed, but because of the aurophilic attractions responsible for stabilizing the clusters, and in some cases deciding their geometry. This hypercoordination has been observed for boron, carbon, nitrogen, phosphorus, sulfur, and oxygen [7]. The gold phosphine units are isolobal with H [2,10], but it is "quite clear that the electronic situation is richer [10a]." This is because of the low-lying p orbitals on gold. CH₆²⁺ is

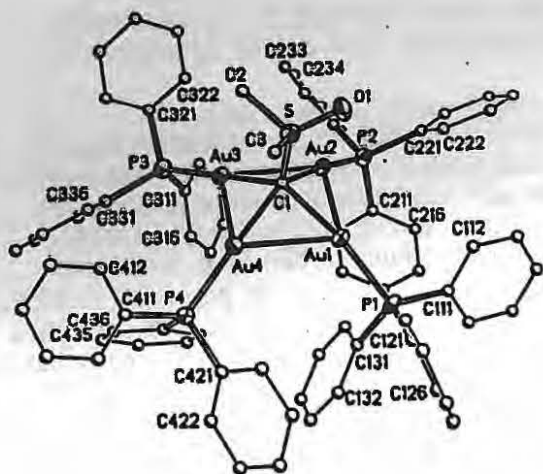


Figure 6

unknown, contrasted with the real octahedral $[(\text{Ph}_3\text{P})\text{Au}]_6\text{C}^{2+}$ cation (Figure 5). The distances between perimeter atoms in these centered clusters is usually from 2.9 to 3.0 angstrom, indicating a significant bonding interaction. It is apparent, also, that in some cases the clusters form to permit this interaction. An example of a cluster forming to permit such interactions is the structure of the square planar cluster of $[(\text{AuPPh}_3)_4\{\mu^4\text{-CS(=O)Me}_2\}](\text{ClO}_4)_2$ (Figure 6). In this structure, the gold units add to the same methyl group despite the steric crowding and more acidic protons on the other methyl groups [11].

References

1. Schoen, G.; Simon, U., "A Fascinating New Field in Colloid Science: Small Ligand-Stabilized Metal Clusters and Possible Application in Microelectronics," *Colloid Polym. Sci.* 1995, 273, 101.
2. Plas, P.V.D.; Leunissen, J.L.M., "Ultrasmlal Gold Probes: Characteristics and Use in Immuno(cyto)chemical Studies," *Meth. Cell Bio.* 1993, 37, 241.
3. Dietrich, G.; Luetzenkirchen, K., "Auⁿ⁺-Induced Decomposition of N₂O," *Ber. Bunsenges. Phys. Chem.* 1994, 98, 1608.
4. (a) Mulder, F.M.; Thiel, R.C.; de Jongh, L.J.; Gubbens P.C.M., "Size-Evolution Towards Metallic Behavior in Nano-Sized Gold and Platinum Clusters as Revealed by ¹⁹⁷Au Mossbauer Spectroscopy," *Nanosrucl. Mat.* 1996, 7, 269.
 (b) Haebleren, O.D.; Chung, S.C; Roesch, Notker, "On the Metallic Droplet Model for Successive Ionization Potentials of Metal Clusters-Relativistic Electronic Structure Investigations of the Icosahedral Gold Cluster Au₅₅," *Ber. Bunsenges. Phys. Chem.* 1994, 98, 882.
 (c) Devenish, R.W.; Goulding, T.; Heaton, B.T.; Whyman, R., "Preparation, Characterisation and Properties of Groups VIII and IB Metal Nanoparticles," *J. Chem. Soc. Dalton Trans.* 1996, 5, 673.
5. Schmidbaur, H., "The Fascinating Implications of New Results in Gold Chemistry," *Gold Bull. and Pat. Digest* 1990, 23, 11.
6. Veiros, L.F.; Calhorda, M.J., "How Bridging Ligands and Neighbouring Groups Tune the Gold-Gold Bond Strength," *J. Organomet. Chem.* 1996, 510, 71.

7. (a) Angermaier, K.; Schmidbaur, H., "Further Gold Aggregation at a Pentanuclear Gold Cluster with Hypercoordinate Interstitial Nitrogen," *Inorg. Chem.* **1995**, *34*, 3120.
- (b) Haerberlen, O.D.; Schmidbaur, H.; Roesch, N., "Stability of Main-Group Element-Centered Gold Cluster Cations," *J. Am. Chem. Soc.* **1994**, *116*, 8241.
- (c) Canales, F.; Gimeno, C.; Laguna, A.; Villacampa, M.D., "Aurophilicity at Sulfur Centers. Synthesis of the Polyaurated Species $[S(AuPR_3)_n]^{(n-2)+}$ ($n=2-6$)," *Inorganica Chim. Acta* **1996**, *244*, 95.
- (d) Li, J.; Pyykkoe, P., "Structure of $E(AuPH_3)^{4+}$, $E = N, P, As$: T_d or C_{4v} ?" *Inorg. Chem.* **1993**, *32*, 2630.
8. (a) Schwerdtfeger, P.; Dolg, M.; Schwarz, W.H. E.; Bowmaker, G.A.; Boyd, P.D.W., "Relativistic Effects in Gold Chemistry. 1. Diatomic Gold Compounds," *J. Chem. Phys.* **1989**, *91*, 1762.
- (b) Norrby, L.J., "Why Is Mercury Liquid?" *J. Chem. Ed.* **1991**, *68*, 111.
9. (a) Briant, C.E.; Hall, K.P.; Wheeler, A.C.; Mingos, D.M.P., "Structural Characterisation of $[Au_{10}Cl_3(PCy_2Ph)_6](NO_3)$ (Cy = cyclohexyl) and the Development of a Structural Principle for High Nuclearity Gold Clusters," *J. Chem. Soc. Chem. Comm.* **1984**, *5*, 248.
- (b) Mingos, D.M.P., "Gold - A Flexible Friend in Cluster Chemistry," *J. Chem. Soc. Dalton Trans.* **1996**, *5*, 561.
10. (a) Burdett, J.K.; Eisenstein, O.; Schweizer, W.B., "Are Strong Gold-Gold Interactions Possible in Main Group $X_nA(AuPR_3)_m$ Molecules?" *Inorg. Chem.* **1994**, *33*, 3261.
- (b) Evans, D.G.; Mingos, D.M.P., "Molecular Orbital Analysis of the Bonding in Low Nuclearity Gold and Platinum Tertiary Phosphine Complexes and the Development of the Isolobal Analogies for the $M(PR_3)$ Fragment," *J. Organomet. Chem.* **1982**, *232*, 171.
- (c) Hoffman, R., "Building Bridges Between Inorganic and Organic Chemistry," *Angewandte Chem. Int. Ed. Eng.* **1982**, *21*, 711.
11. Vicente, J.; Chicote, M.T.; Guerrero, R.; Jones, P.G., "Synthesis of the First Complex with a Hypercoordinate Ylidic Carbon Atom. Crystal and Molecular Structure of $[(Au(PPh_3))_4CS(=O)Me_2](ClO_4)_2$," *J. Am. Chem. Soc.* **1996**, *118*, 699.