

Structure and Bonding in Clusters of Group 11 and 12 Metals

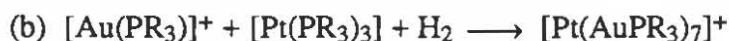
Michael D. Spencer

Literature Seminar

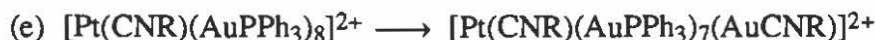
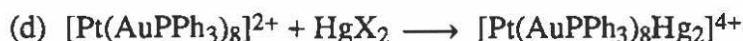
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Transition metal clusters can be viewed as models of metal surfaces and the species present in chemisorption and catalytic processes [1-4]. Clusters have been investigated intensively since the mid 1960s; much of this work has focused on the early and mid transition metals. Clusters of the late transition metals, particularly those of gold and mercury, are known but have been relatively little studied [5,7,8,12c]. Interestingly, these clusters do not follow Wade's rules and the heteronuclear clusters do not always conform to the predictions of the modified Wade's rules introduced by Mingos for homonuclear gold clusters [13].

Heteronuclear gold clusters are synthesized in two principal ways: systematic build-up from smaller clusters (a), or mass assembly from mononuclear precursors (b) [5,6].



Many reactions of gold clusters have been studied; among these are oxidative addition, abstraction of gold by phosphines, deprotonation, addition of $\text{Au}(\text{PR}_3)\text{X}$ species, and ligand exchange reactions (c-g) [7,8].



The reactivity of the central atom is often similar to that of mononuclear complexes of that element.

NMR studies of gold clusters often show that the metal core undergoes fluxional processes. Low temperature NMR studies in solution and in the solid phase do not always yield spectra which are consistent with the solid state structure [9]. FABMS (Fast Atom Bombardment Mass Spectroscopy) has proven useful in the determination of the number of hydrides present in gold clusters, since the parent peak is usually observable. Single crystal X-ray studies have shown that the Au-Au bond lengths vary between 2.6 and 3.1 Å and that the M-Au-P angles are approximately 180 degrees. A wide variety of structures has been determined. The structure of $[\text{Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_7](\text{PF}_6)_2$ was determined to be a centered square prism with one vertex occupied by a phosphine ligand. However, the hydride was not located and the identity of the central metal atom could not be determined from the crystallographic data [6]. The ^{197}Au Mössbauer spectrum of the above cluster showed no singlet at ap-

proximately 3 mm sec^{-1} which is characteristic of gold-centered clusters [6]. Thus, the central metal atom of the cluster was identified as a platinum atom. Mössbauer spectroscopy has also shown that there is a direct relationship between the M-Au bond length and the ^{197}Au isomer shift and quadrupole splitting [10]. Heteronuclear clusters show more resolved Mössbauer spectra than homonuclear clusters because the chemical differences between the inequivalent vertex positions are apparently enhanced [11].

Although Wade's rules can account for the structures of many transition metal clusters [12], they do not successfully predict the structures of heteronuclear gold clusters. Mingos has proposed a modification of Wade's rules, in which the tangential metal-metal bonding is ignored. For a cluster with n vertices, this reduces the number of electrons necessary by $2n$. In his model, there are $(12n + 2)$ electrons for a non-centered spherical cluster and $(12n + 18)$ electrons for centered spherical cluster [13]. Although Mingos' rules are more successful than Wade's rules in accounting for structures of gold clusters, many inconsistencies remain. The actual electron counts frequently fall in between the two predictions with Wade's rules giving electron counts that are too high and Mingos' rules giving electron counts that are too low.

Mason et al. have proposed that metal-metal bonding on the periphery of gold clusters is unimportant and that only radial bonding needs to be considered for structural predictions [14]. In this view, the central atom of the cluster often adopts an 18-electron configuration with the peripheral metal atoms acting as ligands. If the isolobal analogy is used, then the 18-electron rule predicts structures in agreement with those observed experimentally.

There are also some recently reported Hg clusters structures which cannot be accounted for by any electron counting formalism. Among these are various amalgam phases such as $\text{Rb}_{60}\text{Hg}_{64}$ and heterobimetallic clusters such as $\text{Hg}_6\text{Rh}_4(\text{PMe}_3)_{12}$ [15].

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