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Platinum-Gold Cluster Compounds

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Platinum–Gold Cluster Compounds

Platinum–gold cluster compounds with metal frames, consisting of a central Pt surrounded by 5–9 Au atoms have structures and reactivity, governed by a simple 16–18 electron counting rule, like in the case of mononuclear Pt compounds. Structures are toroidal (16 electrons) or spheroidal (18 electrons). The frames are amphoteric in acid–base reactions, preferring CO and RNC as nucleophiles and Au^+, Ag^+ and Cu^+ as electrophilic agents. β-H transfer to form hydrides and oxidative addition, notably with Hg_2X_2 to form $PtAu_8Hg_2$, are known. Clusters with 17 electrons can be prepared by electrochemical reduction and they are relatively stable. Some similarities in structure and reactivity with Pt–Au alloys are shown.

Key Words: *platinum–gold clusters, amphoteric metal clusters, oxidative addition on metal clusters, metal cluster reactivity*

INTRODUCTION

This review deals with structures and reactivity of metal cluster compounds which contain M–L units with M = Cu, Ag and Au and L is a two electron donor ligand, most frequently PPh_3. In recent times many new compounds containing ML have been reported.[1,2] They are of different types:

L'_nM'–(ML), where M′ is Cr, Ir, Pt, Rh and Ru.[1] $[Ir(dppe)_2(AuPPh_3)]^{2+}$ may serve as an example[3] (Fig. 1). Interestingly L–M–M–L compounds have not been detected up until

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now despite several efforts to prepare them and the remarkable stability of Au_2 molecules in the gas phase.

$(L'_n-M')_2$ (μ_2-ML) and $(L'_n-M')_3$ (μ_3-ML), among the many compounds reported, where M' = W, Mn, Fe, Ru, Os, Pt, Re,[4] $Mn_2(\mu_2-AgPEt_3)(\mu_2-PPh_2)(CO)_8$[5] and $Co_3Ru(\mu_3-CuPPh_3)(CO)_{12}$[6] are illustrative examples (Figs. 2 and 3). The isolobal analogy between ML and H has been evidenced and found to be very useful in predicting synthesis and structure of many of these compounds.[7] Conventional electron counting rules, adding up to 16 or 18 electrons, are reliable guides, if the neutral ML moiety is counted as a one-electron donor ligand.

Among the $M'(ML)_x$ compounds, where more than one ML is bonded in the molecule, some (with $x \leq 3$) have structures and electron counts like the above-mentioned categories. In their molecules the ML moieties are spatially well separated, an illustrative example is $Os_3(CO)_{10}(\mu_2-AuPPh_3)_2$[8] (Fig. 4). As compared with $Os_3(CO)_{10}(\mu_2-H)_2$ the isolobal relation still works. In a compound like $[Pt(AuPPh_3)_2Cl(PEt_3)_2](CF_3SO_3)$ and the two $AuPPh_3$ groups are in cis position and the short Au–Au distance of 2.737 Å[9] indicates a strong Au–Au bonding interaction (Fig. 5). The analogous dihydrogen complex $Pt(H_2)Cl(PEt_3)_2^+$ has not been de-

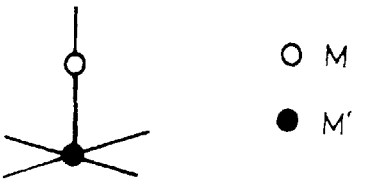


FIGURE 1 $[Ir(dppe)_2(AuPPh_3)]^{2+}$. Only the coordination geometry is shown.

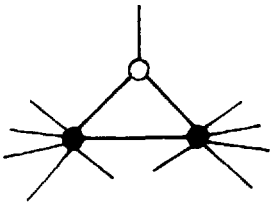


FIGURE 2 $Mn_2(\mu_2-AgPEt_3)(\mu_2-PPh_2))CO)_8$.

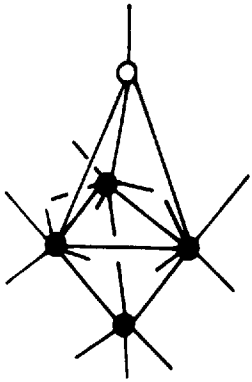


FIGURE 3 $Co_3Ru(\mu_3\text{-}CuPPh_3)(CO)_{12}$.

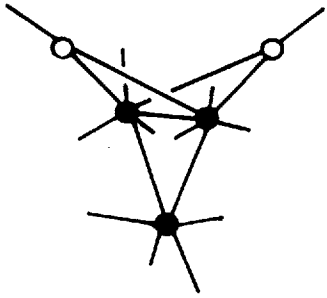


FIGURE 4 $Os_3(CO)_{10}(\mu_2\text{-}AuPPh_3)_2$.

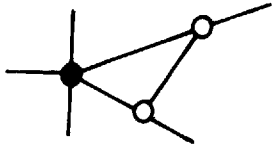


FIGURE 5 $[Pt(AuPPh_3)_2Cl(PEt_3)_2](CF_3SO_3)$.

tected so far. Clusters containing $Au_2(PPh_3)_2$ moieties are considered as isolobal models of dihydrogen complexes.[10] M–M interactions become even more important in a category of cluster compounds $M'(ML)_x$ where $3 \leq x \leq 12$. The present review will deal mainly with this type of compounds.

$M'(AuPPh_3)_x$ CLUSTER COMPOUNDS ($3 \leq x \leq 12$)

Compounds have now been reported where M′ is O, S or Se ($x = 3$),[11-13] N ($x = 4$ or 5),[14,15] P($x = 4$),[16] C ($x = 5$ or 6),[17-19] Au ($7 \leq x \leq 12$),[2] Pd ($x = 8$),[20] Rh ($4 \leq x \leq 8$)[21,22] and Pt (Figs. 6, 7 and 8). In this review we will concentrate on Pt compounds with $6 \leq x \leq 9$. The close Au–Au contacts (between 2.7 and 3.2 Å) in these clusters and in a great variety of other compounds are caused by what has been called "aurophilicity."[18,19] This "philicity" suggests the importance of the Au–Au bonding interactions. In contrast the adjective "porcupine-like," as these compounds were called many years ago,[23] suggested that peripheral interactions were negligible, and only radial bonding was supposed to be important. Today, we know from MO calculations that radial as well as peripheral bonding interactions contribute to the stability of

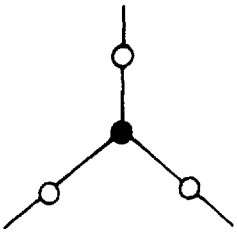


FIGURE 6 $O(AuPPh_3)_3^+$.

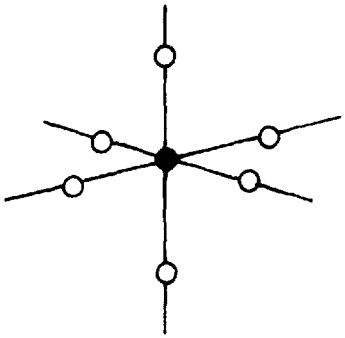


FIGURE 7 $C(AuPPh_3)_6^{2+}$.

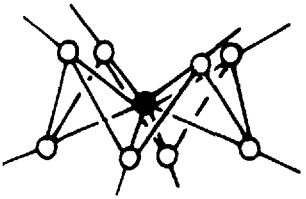


FIGURE 8 $Pt(AuPPh_3)_8^{2+}$.

these compounds. The maximum number of x is 12, which is the coordination number in close packing as well as in icosahedral symmetry. Steric restrictions are further set by the number of ligands L. From a great variety of experimental data and the calculation of the Kitaigorodski coefficient we now know that no more than 8 PPh_3 can be packed around the metal frame.[2]

STRUCTURES

The structures of the metal frames, as determined by X-ray analysis, have attracted much interest. Initially we and others have been focussed much upon the idea of icosahedral fragments to be present. In contrast with cubic or hexagonal close packing in macroscopic crystals of metals, very small metal particles sometimes have icosahedral symmetry. So in this respect they show an interesting analogy with the metal frames in these cluster compounds. Today we know that the electron count determines the main structural characteristic of this type of clusters; 16 or 18 valence electrons in the cluster determines the structure to be toroidal or spheroidal, respectively[24] (when the central atom is a main group element the electron counts are 6 or 8). This is demonstrated in Figs. 9 and 10. This criterium is analogous to the 16 and 18 electron counts in mononuclear transition metal compounds which predict square planar and more spheroidal-like symmetry, respectively. Objective topological criteria have been developed to classify more complex structures as toroidal or spheroidal.[25]

The radial Pt–Au bond lengths are 2.6–2.8 Å and the closest Au–Au distances in the periphery of the metal frame are 2.8–2.9 Å. In the X-ray structure determination Pt and Au can not be

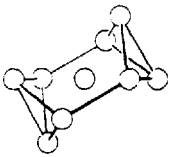


FIGURE 9 $[Au(AuPPh_3)_8]^{3+}$ with toroidal structure and 16 cluster valence electrons.

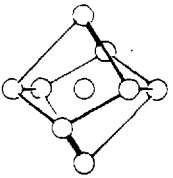


FIGURE 10 $[Au(AuPPh_3)_8]^{+}$ with spheroidal structure and 18 valence electrons. Phosphines and radial interactions are not indicated.

distinguished. So the position of the Pt must be determined by careful analyses of ^{195}Pt and ^{31}P NMR and/or ^{197}Au Mössbauer spectra. Up until now no isomer with a central Au and a peripheral Pt has been detected. They are probably less stable, reminiscent of the surface segregation in Pt–Au alloys, where Pt avoids the surface.

In this review the relevance of the electron counting rules will be demonstrated in the structures, but also in the classification of the reactions of the cluster compounds. Minor structural differences occur within the categories of toroidal and spheroidal. An example is the crown-like and the icosahedral-fragment structure of $[Au(AuPPh_3)_8]^{3+}$, known to be present in isomers of this compound,[26] which have about equal energies and in solution show a rapid interconversion. Many of these cluster compounds show a fast fluxionality in solution that can only be retarded at very low temperatures. Details of metal frame geometry and its fluxionality are not well understood.

REACTIVITY

The chemical reactivity of this type of clusters is varied and the central metal and/or the peripheral Au-L sites may be involved.

The fragmentation and growth of the metal frame as well as the redox reactions will be discussed separately.

AuL Site Reactivity

The nucleophilic substitution of L is demonstrated in the following reactions[27,28]:

$$[Au(AuPPh_3)_8(AuCl)_2]^+ + Cl^- \rightarrow Au(AuPPh_3)_7(AuCl)_3 + PPh_3$$

$$[Au(AuPPh_3)_8]^{3+} + 2CNR \rightarrow [Au(AuPPh_3)_6(AuCNR)_2]^{3+} + 2PPh_3$$

$$[Pt(CO)(AuPPh_3)_8]^{2+} + Cl^- \rightarrow [Pt(CO)(AuPPh_3)_7(AuCl)]^+ + PPh_3$$

Substitution of PPh_3 by $P(p\text{-}ClC_6H_4)_3$ has been observed for Au as well as for Pt centered clusters; at room temperature the substitution is slow on the NMR time scale.[29] Clusters which have different Au–P sites in the crystalline state show only a single Au–P resonance in the ^{31}P NMR spectra at room temperature. So there is an interesting intramolecular fluxionality,[30] which at low temperatures slows down, resulting in more complicated ^{31}P NMR spectra. It is not clear whether there is only migration of PPh_3 over the metal frame or Au atoms are also involved in these processes.

Central Metal Reactivity

Nucleophilic addition reactions at the central metal of clusters which have 16 cluster valence electrons result in 18-e clusters, as shown in[31,32]:

$$[Au(AuPPh_3)_7]^{2+} + PPh_3 \rightleftarrows [Au(PPh_3)(AuPPh_3)_7]^{2+}$$

$$[Pt(PPh_3)(AuPPh_3)_6]^{2+} + CC\text{-}tBu^- \rightarrow [Pt(PPh_3)(CC\text{-}tBu)(AuPPh_3)_6]^+$$

$$[Pt(AuPPh_3)_8]^{2+} + CO \rightarrow [Pt(CO)(AuPPh_3)_8]^{2+}$$

The structure of $[Pt(CO)(AuPPh_3)_8]^{2+}$ is interesting in comparison with that of $[Pt(AuPPh_3)_8]^{2+}$; they are shown in Figs. 11 and 12. CO is attached to the central Pt, which is further bonded to eight Au atoms, giving the Pt a coordination number of nine.[33] The CO causes the $AuPPh_3$ groups to bend downward, changing the toroid-like $[Pt(AuPPh_3)_8]^{2+}$ into a more spherically filled cluster $[Pt(CO)(AuPPh_3)_8]^{2+}$. This is in accord with the change in electron count from 16 to 18. The metal framework of $[Pt(CO)(AuPPh_3)_8]^{2+}$ is reminiscent of the (100) plane of the face-centered cubic lattice of Pt, Au and their alloys. This is shown in Fig. 13, where deviations from the ideal lattice points are indicated in a perspective sketch and a scaled projection on (100). Although the deviations are significant, the overall similarity is striking. The stretching frequencies of CO, adsorbed on various crystal faces of platinum metal, are found at 2060–2125 cm^{-1}. These are assigned to CO adsorbed at steps and terraces. At low coverage of CO on Pt(111), absorptions are found in the range 1810–1860 cm^{-1} and these are

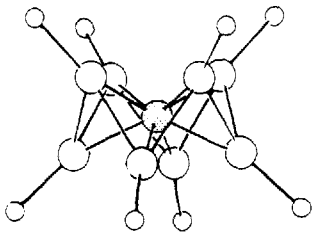


FIGURE 11 $[Pt(AuPPh_3)_8]^{2+}$.

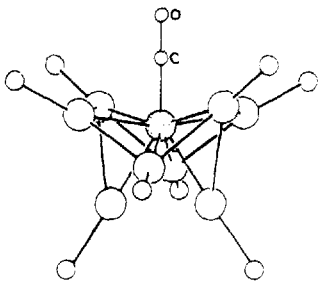


FIGURE 12 $[Pt(CO)(AuPPh_3)_8]^{2+}$.

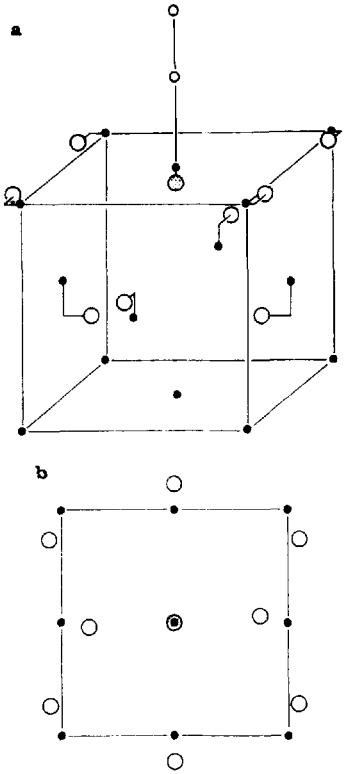


FIGURE 13 The similarity of $[Pt(CO)(AuPPh_3)_8]^{2+}$ and the face-centered cubic lattice of Pt–Au alloys (a) in a perspective view, (b) a scaled projection on (100). ● = ideal lattice point.

assigned to chemisorbed CO in bridges and on sites of threefold symmetry. The stretching frequency for $[Pt(CO)(AuPPh_3)_8]^{2+}$ is at 1940 cm^{-1}, just in between both ranges. PtAu-cluster compounds react with isonitriles in a similar way as they do with CO[34,35]:

$$[Pt(AuPPh_3)_8]^{2+} + CNR \rightarrow [Pt(CNR)(AuPPh_3)_8]^{2+}$$

Hydride containing clusters are formed when after a nucleophilic attack of OCH_3^- a β–H shift occurs and CH_2O is eliminated.

$$[Pt(AuPPh_3)_8]^{2+} + OCH_3^- \rightarrow [Pt(H)(AuPPh_3)_8]^+ + OCH_2$$

$$[Pt(PPh_3)(AuPPh_3)_6]^{2+} + OCH_3^- \rightarrow [Pt(H)(PPh_3)(AuPPh_3)_6]^+ + OCH_2$$

^{195}Pt, ^{31}P and ^1H NMR data give a consistent picture of the structures, where H is believed to be bond very near to the Pt. These hydrides are stable in air but react with dilute acids, consuming one equivalent H^+ to produce H_2 and the parent compounds in nearly 100% yield.[36]

Substitution of a phosphine, bonded to the central Pt, is found to occur with $SnCl_3^-$.

$$[Pt(H)(PPh_3)(AuPPh_3)_7]^{2+} + SnCl_3^- \rightarrow [Pt(H)(SnCl_3)(AuPPh_3)_7^+ + PPh_3$$

^{119}Sn and ^{117}Sn couplings are observed in ^{31}P and ^{195}Pt NMR spectra. The high values of $J(^{195}Pt-^1H)$ (680 Hz) and $J(^{195}Pt-^{117}Sn)$ (8050 Hz) clearly indicate that the central Pt is bonded to H and to $SnCl_3$.[36]

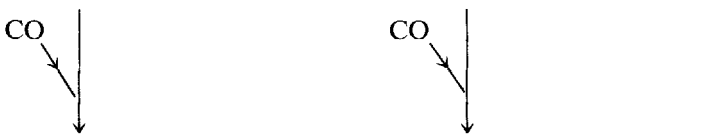
Electrophilic addition on the central atom of the clusters is well documented for Au-centered as well as for Pt-centered clusters with 16 or 18 electrons. Examples are:

$$[Au(AuPPh_3)_7]^{2+} + AuPPh_3^+ \rightarrow [Au(AuPPh_3)_8]^{3+}$$

$$[Pt(H)(PPh_3)(AuPPh_3)_6]^+ + AuPPh_3^+ \rightarrow [Pt(H)(PPh_3)(AuPPh_3)_7^{2+}$$

Particularly interesting are the additions of Ag^+ and Cu^+.[37]

$$[Pt(AuPPh_3)_8]^{2+} + MX \rightarrow [Pt(MX)(AuPPh_3)_8]^{2+}$$



with M = Ag, X = Cl, NO_3 and M = Cu, X = Cl. The $AgNO_3$ adduct dissociates its NO_3^- in solution, leaving $[Pt(Ag)(AuPPh_3)_8]^{3+}$ with an exposed Ag as well as a coordinatively unsaturated Pt (16 electron cluster). The structures of the cationic clusters of the $AgNO_3$ adducts are shown in Fig. 14. Two Cu or Ag can be incorporated in the periphery of the cluster after expulsion of one of the bulky $AuPPh_3$-groups.[38]

$$[Pt(CO)(AuPPh_3)_8]^{2+} + 2\,MX + PPh_3 \rightarrow Au(PPh_3)_2^+ + [Pt(CO)(AuPPh_3)_8(MX)_2]^+$$

The Pt center is obviously amphoteric and soft, like mononuclear Pt compounds which prefer soft acids like Ag^+ and Hg^+ and soft bases like CO and PR_3.

Brönsted base behavior is now known only for some electron-rich (18-e) Pt centered clusters. The reaction:

$$[Pt(PPh_3)(AuPPh_3)_7]^+ + H^+ \rightleftarrows [Pt(H)(PPh_3)(AuPPh_3)_7]^{2+}$$

is supposed to be a step[39] in the reversible process:

$$[Pt(AuPPh_3)_8]^{2+} + H^+ + PPh_3 \rightleftarrows [Pt(H)(PPh_3)(AuPPh_3)_7]^{2+} + AuPPh_3^+$$

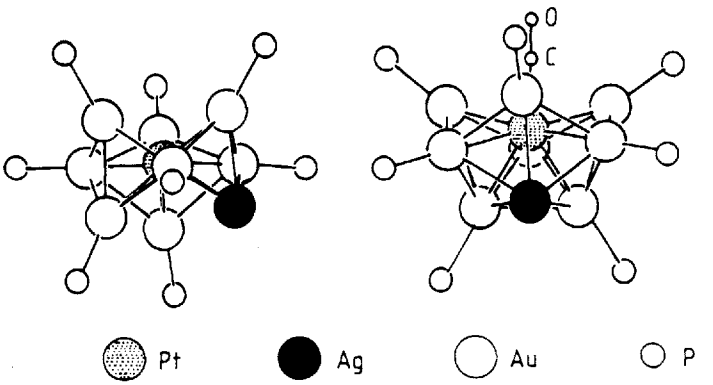


FIGURE 14 Comparison of the structures of $[Pt(AgNO_3)(AuPPh_3)_8](NO_3)_2$ and $[Pt(CO)(AgNO_3)(AuPPh_3)_8](NO_3)_2$ showing the change in the metal frame caused by the addition of CO.

The reaction product $[Pt(H)(PPh_3)(AuPPh_3)_7]^{2+}$ is a stable, weakly acidic compound.[40] It reacts with an excess of acid and is then converted into $[Pt(PPh_3)(AuPPh_3)_6]^{2+}$.

$$[Pt(H)(PPh_3)(AuPPh_3)_7]^{2+} + H^+ \rightarrow H_2 + [Pt(PPh_3)(AuPPh_3)_6]^{2+} + AuPPh_3^+$$

Compounds with 2H in the cluster apparently can not survive the intermediate and eliminate H_2 to form 16-e clusters which are weak bases that resist further attack by H^+. Recently a Rh-centered cluster has been reported,[21] where two hydrides are bonded on a stable $Rh(H)_2Au_4$-frame. Although $Au(H)_y(AuL)_x$ clusters should be intermediates in the synthesis of $Au(AuL)_x$ clusters from AuL^+ and H_2, up until now no hydride containing cluster of that type has been detected. In general there is a greater variation in the chemistry of $Pt(AuPPh_3)_x$ than of $Au(AuPPh_3)_x$ clusters, like the chemistry of mononuclear Pt complexes being much more varied than that of mononuclear Au compounds. Relevant examples are the great number of stable Pt(CO) and Pt(H) complexes compared with the instability of the few known Au(CO) and Au(H) complexes.

Oxidative additions and reductive elimination reactions are reactions where the coordination number changes by 2, concomitant with a change of 2 in the electron count (16–18). This is in analogy with the common use of this terminology for reactions of mononuclear compounds of transition metals, irrespective of the precise mechanism. Some examples[41,42] for the cluster compounds are:

$$[Pt(AuPPh_3)_8]^{2+} + Au(CN)_2^- \rightarrow [Pt(CN)(AuCN)(AuPPh_3)_8]^+$$

$$[Pt(AuPPh_3)_8]^{2+} + Hg_2X_2 \rightarrow [Pt(AuPPh_3)_8(HgX)_2]^{2+}$$

Most interesting is the oxidative addition of Hg_2X_2 (X = NO_3, Cl or Br) to $[Pt(AuPPh_3)_8]^{2+}$, which yields a $PtAu_8Hg_2$-frame.[42] When X = NO_3, the nitrate dissociates in polar solutions. Crystalline

compounds were obtained with and without NO_3 coordinated to the Hg atoms. The X-ray structure of $[Pt(AuPPh_3)_8(Hg)_2]^{4+}$ shows two Hg atoms in trans position and the crown configuration of the parent $PtAu_8$ is nearly unaffected (Fig. 15). As the PtAu frames are highly fluxional, the primary reaction product of the oxidative addition could be different from what is found in the crystalline state. A conclusion about the reaction mechanism therefore seems premature. The substitution of the Hg-bonded NO_3^- by Cl^- is a fast reaction. That is also true for the substitution of one of the Au-bonded phosphines by nitrate or chloride, yielding $[Pt(AuPPh_3)_7(AuX)(HgX)_2]^+$ with X = NO_3 or Cl. The driving force of these reactions is the steric crowding of the eight phosphines in combination with a coordination as high as 10 for the central Pt. The steric strain can also be removed by dissociation of one of the $AuPPh_3$-groups:

$$[Pt(AuPPh_3)_8(HgX)_2] \rightarrow [Pt(AuPPh_3)_7(HgX)_2]^+ + AuPPh_3^+$$

This equilibrium can be shifted to the right by addition of PPh_3, which binds the $AuPPh_3^+$ as $Au(PPh_3)_2^+$.

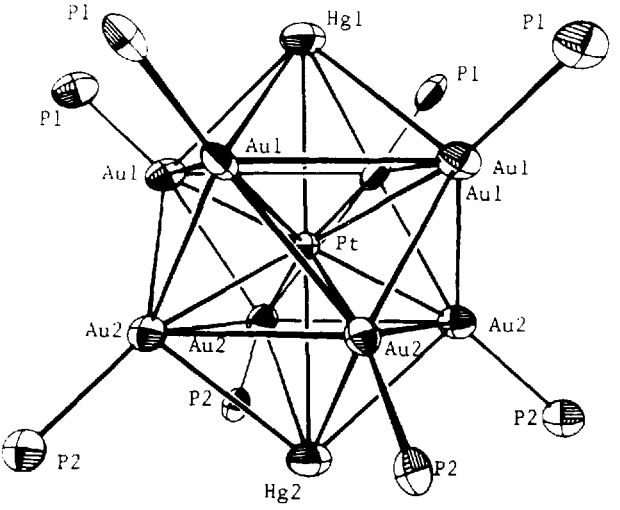


FIGURE 15 $[Pt(AuPPh_3)_8Hg_2]^{4+}$ in the crystalline nitrate.

Redox Reactions

Redox reactions can be studied successfully with electrochemical methods where 16 and 18 electron clusters show characteristic patterns.[43,44] The reduction of $M'(AuPPh_3)_8$ (16-e) proceeds via two reversible one-electron steps, at potentials depending on M'. $E_{1/2}(Au) > E_{1/2}(Pt) > E_{1/2}(Pd)$. This is the same order as found for the reduction potentials of mononuclear Au, Pt and Pd compounds. The relative stability of the 17-electron species, as indicated by the difference in $E_{1/2}$ of the two consecutive reduction steps of 100 mV, is unprecedented in mononuclear compounds of Au, Pt and Pd. However, comproportionations are fast, so the 17-electron clusters could not be isolated as pure compounds. Oxidation of 16 electron clusters leads to irreversible fragmentation of the cluster. Thus, less than 16 electron and more than 18 electron systems cannot be achieved. Oxidations of stable 18-e clusters are irreversible, which is probably due to problems with the accommodation of the many ligands in a toroid-like structure, demanded by the 16 electrons of the oxidized form.

Fragmentation and Growth of Metal Frame

The synthesis of the cluster compounds from mononuclear metal compounds can be achieved with reducing agents like $NaBH_4$, B_2H_6, $Ti(\eta\text{-}C_6H_5CH_3)_2$[7] and also in fast reactions with H_2 or CO/H_2O at atmospheric pressure and room temperature.[34] A series of hydride transfers ($NaBH_4$) or oxidative additions of H_2 and electrophilic substitutions is supposed to be operative:

$$M'(L)(ML)_x + H^- \rightarrow M'(H)(L)(ML)_x^-$$

or

$$M'(L)(ML)_x + H_2 \rightarrow M'(H)_2(L)(ML)_x$$

$$M'(H)(L)(ML)_x + ML^+ \rightarrow M'(L)(ML)_{x+1} + H^+, \text{ etc.}$$

Growth can also occur by electrophilic or oxidative additions as described above the corresponding paragraphs.

When in a 16-e $M'(AuL)_x$ x increases, steric crowding in the toroid could finally prohibit further growth of the cluster unless spheroidal coordination around the center becomes possible. Then two more electrons are needed to reach the 18-electron configu-

ration. In this respect there is an interesting difference between Pt and Au centered clusters. For M′ = Au the oxidation potential is high so a redox disproportionation can occur, leaving a part of the cluster reduced and ready for further growth and another part oxidized, fragmenting finally to mononuclear Au(I) or Au(III) complexes. The following reaction[27] is important in synthetic routes (X = Cl, Br, SCN):

$$[Au(AuPPh_3)_8]^{3+} + 2AuX \rightarrow Au(AuPPh_3)_8(AuX)_2^+ + \text{oxidized products.}$$

For M′ = Pt the oxidation potential is too low for the redox disproportionation to occur. When a base B (B = CO, CNR, H^-, CN^-) is present in solution, growth can proceed after nucleophilic addition of the base which provides the 2 extra electrons needed:

$$[Pt(AuPPh_3)_8]^{2+} + B + AuX \rightarrow [Pt(B)(AuPPh_3)_8(AuX)]^{2+}$$

Shrinking the metal frame by decreasing x in $M'(ML)_x$ is sometimes an interesting route in the synthesis. It is known[27,38] that it can be induced by nucleophilic attack followed by reductive elimination:

$$[Au(AuPPh_3)_8]^{3+} + PPh_3 \rightarrow Au(AuPPh_3)_7^{2+} + Au(PPh_3)_2^+$$

The final products of growth and fragmentation in synthetic routes critically depend upon the nature and the concentration of ligating agents present in the solution (phosphines, Cl^-, SCN^-, etc.). $AuPPh_3^+$ and $Pt(PPh_3)_3$ are obvious starting materials for the synthesis as they are stable and easily accessible compounds. However, a high phosphine/metal ratio limits the products to clusters with a high phosphine content. Therefore we have explored Pt precursors without phosphines. As Pt complexes are generally substitution inert, we have looked for new Pt compounds with cyclo-octadiene as ligand as we think this to be an easily leaving ligand and suitable in the synthesis of clusters.[45]

The variety of the central atom M′ that is known today (O, S, Se, N, P, C, Au, Pd, Rh, and Pt) raises the expectation that many other central atoms may give stable compounds, including main group elements like B as well as transition metals. How great the variety of M′ may be, until now M is mainly restricted to Au. Only a few compounds are known with one or two Ag, Cu or Hg among seven or eight Au attached to the central Pt. However, in the more

complicated "superclusters," which are vertex-sharing centered icosahedral clusters, up to 6 Ag atoms per icosahedron with short Ag–Ag contacts are present.[46] So future efforts to synthesize $M'(AuL)_x(ML)_y$ with M = Ag, Cu or Hg and with $y > 2$ might be successful.

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References

1. A. M. Mueting, W. Bos, B. D. Alexander, P. D. Boyle, J. A. Casalnuovo, S. Balaban, L. N. Ito, S. M. Johnson and L. H. Pignolet, New J. Chem. **12**, 505 (1988) and references therein.
2. J. J. Steggerda, J. J. Bour and J. W. A. van der Velden, Recl. Trav. Chim. Pays-Bas **101**, 164 (1982).
3. A. L. Casalnuovo, T. Laska, P. V. Nilsson, J. Olofson and L. H. Pignolet, Inorg. Chem. **24**, 233 (1985).
4. I. D. Salter, *Advances in Organometall. Chemistry* (Academic Press, London, 1989, Vol. 29, p. 249) and references therein.
5. J. A. Iggo, M. J. Mays, P. R. Raithby and K. Henrick, J. Chem. Soc. Dalton Trans. 633 (1984).
6. P. Braunstein, J. Rosé, A. Dedieu, Y. Dusausoy, J. P. Maugeot, A. Tiripicchio and M. Tiripicchio-Camellini, J. Chem. Soc. Dalton Trans. 225 (1986).
7. K. P. Hall and D. M. P. Mingos, *Progress in Inorganic Chemistry* Vol. 32. (John Wiley and Sons, New York, 1984).
8. K. Burgers, B. F. G. Johnson, D. A. Kaner, J. Lewis, P. R. Raithby and S. N. A. B. Syed-Mustaffa, J. Chem. Soc. Chem. Commun. 455 (1983).
9. P. Braunstein, H. Lehner, D. Matt, A. Tiripicchio and M. Tiripicchio-Camellini, Angew. Chem. Int. Ed. Engl. **23**, 304 (1984).
10. M. Bruce, P. Corbin, P. Humphrey, G. Koutsantonis, M. Liddell and E. Tiekink, J. Chem. Soc. Chem. Commun. 674 (1990).
11. A. N. Nesmeyanov, G. G. Perevalova, Y. T. Struchkov, M. Y. Antipin, K. I. Grandberg and V. P. Dyadchenko, J. Organometal. Chem. **201**, 343 (1980).
12. C. Lensch, P. G. Jones and G. M. Sheldrick, Z. Naturforsch. B **37**, 944 (1982).
13. P. G. Jones, C. Lensch and G. M. Sheldrick, Z. Naturforsch. B **37**, 141 (1982).
14. Y. L. Shlovokhotov and Y. T. Struchkov, J. Organometal. Chem. **277**, 143 (1984).
15. A. Grohman, J. Riede and H. Schmidbauer, Nature **345**, 140 (1990).
16. W. Kress, Diss., Univ. Erlangen-Nürnberg (1983).
17. F. Scherbaum, A. Grohman, G. Muller and H. Schmidbaur, Angew. Chem. **101**, 464 (1989).
18. F. Scherbaum, A. Grohman, B. Huber, C. Kruger and H. Schmidbauer, Angew. Chem. **100**, 1602 (1988).
19. H. Schmidbauer, Gold Bull. **23**, 11 (1990).
20. L. N. Ito, B. J. Johnson, A. M. Mueting and L. H. Pignolet, Inorg. Chem. **28**, 2028 (1989).

21. B. D. Alexander, A. M. Mueting and L. H. Pignolet, Inorg. Chem. **29**, 1313 (1990).
22. S. G. Bott, M. P. Mingos and M. J. Watson, J. Chem. Soc. Chem. Commun. 1192 (1989).
23. R. B. King, *Progress in Inorganic Chemistry*, Vol. 15 (John Wiley and Sons, New York, 1972), p. 287.
24. D. M. P. Mingos, Polyhedron **3**, 1289 (1984).
25. R. P. F. Kanters and J. J. Steggerda, J. Cluster Sc., in press.
26. K. P. Hall, B. R. C. Theobald, D. I. Gilmour, D. M. P. Mingos and A. J. Welch, J. Chem. Soc. Chem. Commun. 528 (1982).
27. F. A. Vollenbroek, J. J. Bour and J. W. A. van der Velden, Recl. Trav. Chim. Pays-Bas **99**, 137 (1980).
28. W. Bos, J. J. Bour, J. W. A. van der Velden, J. J. Steggerda, A. L. Casalnuovo and L. H. Pignolet, J. Organomet. Chem. **253**, C64 (1983).
29. F. A. Vollenbroek, J. P. van den Berg, J. W. A. van der Velden and J. J. Bour, Inorg. Chem. **19**, 2685 (1980).
30. R. P. F. Kanters and J. J. Steggerda *et al.*, to be published.
31. J. W. A. van der Velden, J. J. Bour, W. P. Bosman and J. H. Noordik, Inorg. Chem. **22**, 1319 (1983).
32. P. D. Boyle, B. J. Johnson, B. D. Alexander, J. A. Casalnuovo, P. R. Gannon, S. M. Johnson, E. A. Larka, A. M. Mueting and L. H. Pignolet, Inorg. Chem. **26**, 1346 (1987).
33. R. P. F. Kanters, P. P. J. Schlebos, J. J. Bour, W. P. Bosman, H. J. Behm and J. J. Steggerda, Inorg. Chem. **27**, 4034 (1988).
34. R. P. F. Kanters, J. J. Bour, P. P. J. Schlebos and J. J. Steggerda, J. Chem. Soc. Chem. Commun. 1634 (1988).
35. R. P. F. Kanters, P. P. J. Schlebos, J. J. Bour, J. Wijnhoven, E. van den Berg and J. J. Steggerda, J. Organomet. Chem. **388**, 233 (1990).
36. J. J. Bour, Thesis, Nijmegen, 1990.
37. R. P. F. Kanters, P. J. J. Schlebos, J. J. Bour, W. P. Bosman, J. M. M. Smits, P. T. Beurskens and J. J. Steggerda, Inorg. Chem. **29**, 324 (1990).
38. M. F. J. Schoondergang and J. J. Steggerda *et al.*, to be published.
39. J. J. Bour, R. P. F. Kanters, P. P. J. Schlebos, W. P. Bosman, H. Behm, P. T. Beurskens and J. J. Steggerda, Recl. Trav. Chim. Pays-Bas **106**, 157 (1987).
40. R. P. F. Kanters, J. J. Bour, P. P. J. Schlebos, W. P. Bosman, H. Behm, J. J. Steggerda, L. N. Ito and L. H. Pignolet, Inorg. Chem. **28**, 2591 (1989).
41. J. J. Bour, P. P. J. Schlebos, R. P. F. Kanters, W. P. Bosman, J. M. M. Smits, P. T. Beurskens and J. J. Steggerda, Inorg. Chim. Acta **171**, 177 (1990).
42. J. J. Bour, W. van den Berg, P. P. J. Schlebos, R. P. F. Kanters, M. F. J. Schoondergang, W. P. Bosman, J. J. M. Smits, P. T. Beurskens, J. J. Steggerda and P. van der Sluis, Inorg. Chem. **29**, 2971 (1990).
43. J. G. M. van der Linden, M. L. H. Paulussen and J. E. J. Schmitz, J. Am. Chem. Soc. **105**, 1903 (1983).
44. J. G. M. van der Linden, A. M. Roelofsen and G. H. W. Ipskamp, Inorg. Chem. **28**, 967 (1989).
45. F. de Jong, J. J. Bour and P. P. J. Schlebos, Inorg. Chim. Acta **154**, 89 (1988).
46. B. K. Teo and K. Keating, J. Am. Chem. Soc. **106**, 2224 (1984).