

## Ligated Nano-Sized Clusters of Transition Metals and Post-Transition Metals; Their Syntheses and Characterizations

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Metal cluster chemistry has been of great interest in both physics and chemistry recently, due to the intermediate position metal clusters occupy between a metal atom and a bulk metal. Metal clusters are useful as models of catalytic processes, as actual catalysts in some cases, as possible precursors to amorphous metals, and as sources of size specific data for developing a unifying theory which can describe the properties of both metal atoms and bulk metals.

Recent developments in bare metal cluster chemistry have produced some intriguing results. Physical properties (ionization potential, electron affinity, magnetic susceptibility, etc.) show discontinuous behavior as the size of the metal cluster increases (Figure 1) [1]. Such discontinuities might be caused by an abrupt change to a closest-packed structure at a particular cluster size. On the basis of theoretical calculations, it is generally believed that such a change in structure occurs at a cluster size of between  $M_{55}$  and  $M_{100}$ . Above that point, the cluster would behave like bulk metal both physically (ionization potential, electron affinity, magnetic susceptibility) and chemically (reactivity). Gas phase studies of the reaction of Nb and Fe clusters with  $H_2$  (Figure 2) have implied that the ionization potential, along with the structure of these clusters, is correlated with the reactivity [1c, 2].

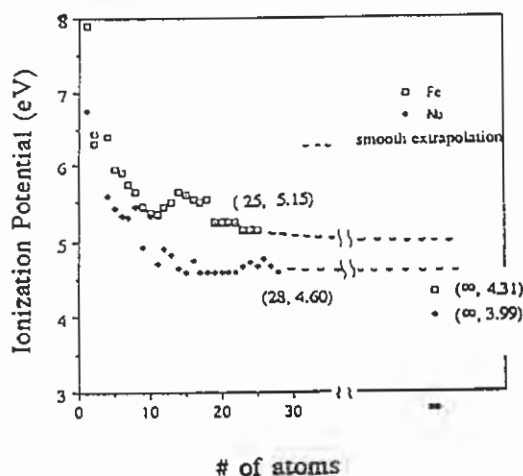


Figure 1. Ionization potential(eV) versus cluster size

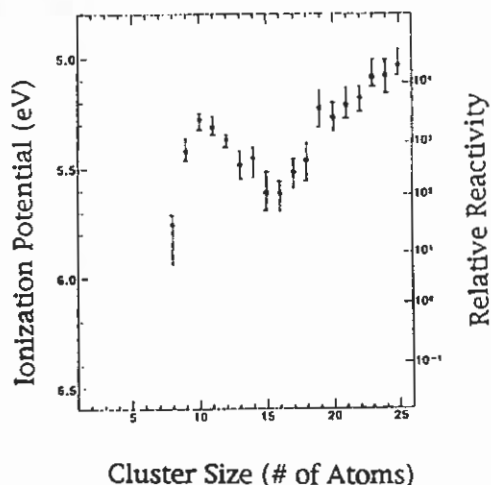


Figure 2. Comparison of measured ionization potential (left-hand scale) with relative reactivities of Fe clusters (right hand scale)

Even though the chemistry of bare metal clusters has provided much useful information which is inaccessible through the study of ligated clusters, further investigations of large bare metal clusters are severely hampered by the absence of a high yield synthetic route and by the difficulty in probing the structures of bare metal clusters with current technology. Accordingly, research is turning increasingly toward studies of large "clothed" metal clusters. The reactivity of these clusters should increase with increasing cluster size, but will also be affected by the nature of the ligands present. The syntheses and chemical and physical properties of these "clothed" metal clusters are discussed below.

Large clothed (ligated) clusters have been prepared in several ways:

- A. Reduction of the appropriate metal salt (e.g.,  $\text{Pd}(\text{OAc})_2$ ) in the presence of protecting ligands (e.g.,  $\text{PR}_3$ , phenanthroline) generating an onion-like metal core coated by ligands; the choice of the reductant and the protecting group is essential [3],
- B. Reaction of a metal halide with a silylated group 15 compound  $\text{ER}(\text{SiMe}_3)_2$  ( $\text{R} = \text{Ph, Me, Et}$ ;  $\text{E} = \text{P, As, Sb}$ ) or a group 16 compound  $\text{E}(\text{SiMe}_3)_2$  ( $\text{E} = \text{S, Se, Te}$ ) generating volatile  $\text{Me}_3\text{SiX}$  [4],
- C. Condensation of a cation with an anion (e.g.,  $\text{Ni}_6(\text{CO})_{12}^{2-}$  with  $\text{PtCl}_2$ ) [5],
- D. Pyrolysis of a smaller cluster (e.g.,  $\text{Pt}_{19}(\text{CO})_{22}^{4-}$  from  $\text{Pt}_9(\text{CO})_{18}^{2-}$ ) [5]

Methods A, B and C, which involve mild reaction conditions, are useful for generating large clusters, but so far do not allow control of the cluster size. On the other hand, method D, which involves rather severe reaction conditions, can control the size of the cluster but often fails in generating very large clusters perhaps due to the instability of such clusters at high temperature.

STM and HRTEM have been useful for determining the structure of large onion clusters prepared by method A. HRTEM gives information about the size and structure of the cluster nucleus, and STM can image the ligands. For other clusters, X-ray crystallography has been used whenever possible. The structures elucidated so far show that closest packing (fcc or ccp) is the common structural theme for these large clusters. This finding supports the idea that ligand field effects are very important in determining the cluster structure. For example,  $\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6$  seems to have a cuboctahedral structure whereas a theoretical study predicts an icosahedral structure for a  $\text{M}_{55}$  bare metal cluster [6].

The magnetic susceptibility of  $\text{Pd}_{561}(\text{phen})_{36}\text{O}_{200}$  (five shells) (Figure 3) was measured and compared with the calculated values for bulk Pd, scaled up for  $\text{Pd}_{561}$  and  $\text{Pd}_{309}$  (four shells) and it matched well with  $\text{Pd}_{309}$  (Figure 4) [7]. Also, a theoretical calculation done on  $\text{Ni}_{44}(\text{CO})_{48}^{n-}$  (an imaginary compound used to model the known compound  $\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}^{n-}$ ) shows that this molecule possesses a magnetic moment due to the inner  $\text{Pt}_6$  metal core. This study shows that the magnetism of the outer Ni atoms is quenched by CO ligands and that the inner core atoms are little affected by the ligands [8]. Therefore, an n-shell clothed metal cluster can be regarded as having an (n-1) shell bare metal cluster at its center, thus possessing physical properties due to that inner cluster.

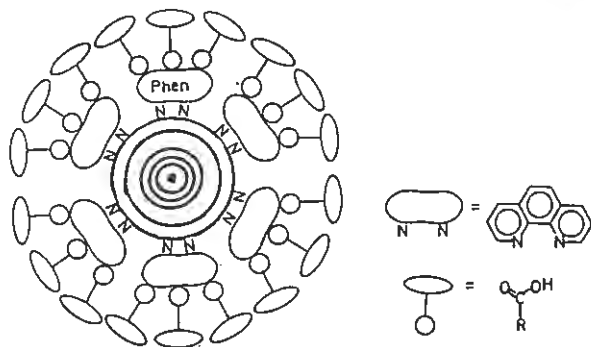


Figure 3. Schematically drawn  $\text{Pd}_{561}\text{Phen}_{36}\text{O}_{200}$  with a second shell of a carbonic acid.

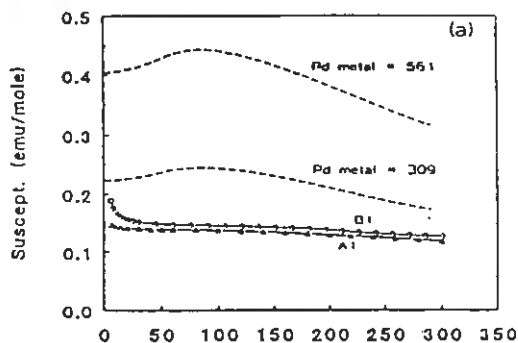


Figure 4. Susceptibility of two different samples of  $\text{Pd}_{561}\text{Phen}_{36}\text{O}_{200}$  versus the calculated curves for bulk Pd, scaled up for  $\text{Pd}_{561}$  and  $\text{Pd}_{309}$

Various  $M_{55}(PPh_3)_{12}Cl_6$  clusters decompose in  $CH_2Cl_2$  when 20 V dc was applied, forming a thermally unstable supercluster  $[(M_{13})_{13}]_n$  [9]. X-ray powder diffraction suggests that the  $M_{13}$  units are linked via triangular faces. This structure is strongly reminiscent of the motif seen in the amorphous portion of supercooled molten Al-Mn alloys [10]. Also, the thermolysis of  $Cu_{70}Se_{35}(PEt_3)_{22}$  has been studied, which showed that it converts via an unknown phase to  $\beta$ - $Cu_2Se$  [11].

Pd onion clusters (31.5 Å and 36 Å in diameter) supported on  $TiO_2$  showed better selectivity for hydrogenation of 1-hexene at 20 °C and 1 atm  $H_2$  than the conventional Pd catalyst (5% Pd on  $Al_2O_3$ ): 100 % conversion versus 58 % ca. conversion. Such selectivity is explained by the relatively narrower size distribution of Pd clusters than is present in the conventional catalyst. It would be interesting to see what surface geometries are abundant in this size range and which is responsible for the hydrogenation activity. Attempts to use  $M_{55}$  onion clusters as homogeneous catalysts for hydroformylation were frustrated due to the decomposition of these clusters in solution [4, 12].

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